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- (71) Applicant (*for all designated States except US*): **RAMOT UNIVERSITY AUTHORITY FOR APPLIED RESEARCH AND INDUSTRIAL DEVELOPMENT LTD.** [IL/IL]; P.O. Box 39296, 61392 Tel Aviv (IL).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **PELED, Emanuel** [IL/IL]; 25 Hanotea Street, 40500 Even Yehuda (IL). **DUVDEVANI, Tair** [IL/IL]; 19 Carmeli Street, 52233 Ramat Gan (IL). **MELMAN, Avi** [IL/IL]; 30 Kdoshei Kahir Street, 58362 Holon (IL). **AHARON, Adi** [IL/IL]; 57 Hagana Street, 46325 Herzliya (IL).
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(54) Title: FUEL CELL WITH PROTON CONDUCTING MEMBRANE

(57) Abstract: The present invention provides improved, low-cost fuel cells having reduced fuel crossover, reduced sensitivity to metal ion impurities and ability to operate under a broad range of temperatures. The invention further provides improved methods for catalyst preparation and a new integrated flow field system for use in H₂/O₂ fuel cells.

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FUEL CELL WITH PROTON CONDUCTING MEMBRANE

FIELD OF THE INVENTION

This invention relates to an electric cell that converts the chemical energy obtained in a fuel oxidation reaction directly into electric energy in a continuous process. More specifically the invention relates to fuel cells.

5 BACKGROUND OF THE INVENTION

Fuel cells are often described as continuously operating batteries or as electrochemical engines. Fuel cells utilize an external supply of fuel and oxygen (or air) and produce power continuously, as long as the fuel and oxygen supply is maintained.

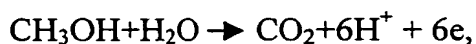
10 The most classic fuel cell is the H_2/O_2 fuel cell of the direct or indirect type, wherein hydrogen is oxidized to form H_3O^+ at the anode and oxygen is reduced to water at the cathode. In the direct type, hydrogen and oxygen are used as such, the fuel being produced in independent installations. The indirect type employs a hydrogen-generating unit, which can use as raw material a wide variety of fuels.

15 Another type of fuel cell is the organic fuel cell. In a direct oxidation cell an aqueous solution of an organic fuel such as methanol, formaldehyde or formic acid, is directly fed into the fuel cell without any previous chemical modification, where the fuel is oxidized at the anode, and oxygen is reduced to water at the cathode.

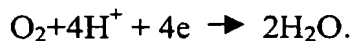
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A major distinguishing characteristic of different fuel cells is in the electrolyte used. NASA's Jet Propulsion Laboratory (JPL) developed a direct liquid-feed cell using a solid membrane electrolyte. A detailed description of JPL's fuel cells can be found, for example, in U.S. Patent Nos. 5,599,638 and 5,773,162.

5 These fuel cells operate without any acid electrolyte and comprise solid electrolyte membranes fabricated from proton-exchange materials, especially NafionTM (manufactured by DuPont). When methanol is used as the fuel, the electro-oxidation of methanol at the anode can be represented by:



10 and the electro-reduction of oxygen at the cathode can be represented by :



Protons generated at the anode are transported directly across the electrolyte membrane to the cathode. A flow of current is sustained by a flow of ions through the cell and electrons through the external load.

15

SUMMARY OF THE INVENTION

The challenge in fuel cell development for practical applications is to improve the economics through the use of low-cost components with acceptable
20 life and performance.

Thus, the present invention provides by the first of its aspects a fuel cell comprising an anode chamber including an anode and means for providing fuel to the anode, a cathode chamber including a cathode and means for providing oxygen to the cathode, and a solid electrolyte membrane disposed between said cathode
25 and said anode, wherein said solid electrolyte membrane is a proton conducting membrane having pores with a diameter, smaller than 30 nm, said membrane comprising:

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- (i) 5% to 60% by volume, preferably 8% to 30% by volume of an electrically nonconductive inorganic powder having a good acid absorption capacity, said powder comprising nanosize particles;
- (ii) 10% to 90% by volume, preferably 30% to 80% by volume of an acid or aqueous acid solution; and
- (iii) 5% to 50% by volume, preferably 12% to 40% by volume of a polymeric binder that is chemically compatible with said acid, oxygen and said fuel.

Typically, when the fuel used is organic, it is provided as a fuel aqueous solution.

The solid proton conducting membrane used in the fuel cells of the present invention has been described in WO 99/44245. The polymeric binders used in these membranes may be selected from the group consisting of poly(vinylidene fluoride), poly(vinylidene fluoride)hexafluoropropylene, poly(tetrafluoroethylene), poly(methyl methacrylate), poly(sulfoneamide), poly(acrylamide), poly(vinylchloride), acrylonitrile, poly(vinyl fluoride), Kel FTM and any combinations thereof.

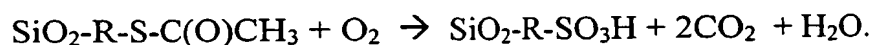
The inorganic nanosize powder used for preparing the solid proton conducting membrane may be selected from the group consisting of SiO₂, ZrO₂, B₂O₃, TiO₂, Al₂O₃, hydroxides and oxy- hydroxydes of Ti, Al, B and Zr, and any combinations thereof.

As described above, the proton conducting membrane used in the fuel cell of the invention comprises, *inter alia*, an acid. Typically, the diameter of the membrane pores is smaller than 30nm, preferably smaller than 3 nm, more preferably smaller than 1.5 nm. As opposed to the solid electrolyte membrane described for example in U.S. Patent No. 5,599,638, wherein no acid is present in free form, the solid electrolyte membrane used in the fuel cell of present invention contains free acid molecules entrapped in the pores of the membrane. Alternatively, it may contain acid molecules bonded to the inorganic powder.

Thus, such a PCM comprises a matrix made of silica powder, preferably nanopowder, bonded with an appropriate polymer binder described above, and

acid molecules chemically bonded to the silica, thus reducing or avoiding the need to insert acid into the fuel solution. Other nanopowders can be used in a similar way. According to this option the acid, preferably sulfonic acid, is chemically bonded to the inorganic nanopowder directly or through an organic
5 segment R selected from $-(CH_2)_n-$, $-(CF_2)_n-$, $-(CF_2CH_2)_m-$, where n is an integer from 1 to 10 and m is an integer from 1 to 5, perfluoroaryl, polyfluoroaryl, perfluorostyrene, polyfluoro styrene and similar segments where up to 50 % of the hydrogen or fluorine atoms were replaced by chlorine atoms.

A non limiting procedure to form sulfonic acid groups bonded to silica is
10 described hereinbelow: nano size silica powder is boiled in pure water for two hours to enrich the powder surface with OH groups. Then the hydrated powder is immersed in a solution of chloro, methoxy, or alkoxy organo sulfur silan of the type $CH_3COSR-Si(OCH_3)_3$ or $CH_3COSR-SiCl_3$, where R is one of the organic segments listed above. The silan reacts with the surface OH groups of the silica
15 powder to form up to one monolayer of the organic sulfur silan. Then the powder is oxidized by air and the thioacetat group is converted into a sulfonic acid group. This step is described in the following equation:



The obtained chemically bonded sulfonic acid is stable in strong acids at
20 90 °C and, therefore, it may be used in the preparation of a PCM for fuel cell applications, instead of pristine SiO_2 .

The anode and the cathode comprise a catalyst layer and optionally also a porous backing layer. A preferred catalyst used at the anode is for example nano size platinum-ruthenium powder, while preferred catalysts used at the cathode are
25 for example nano size platinum powder and alloys thereof with non noble metals, for example Ni, Co, and Fe. In such alloys the ratio between platinum and the metal (Pt:M atomic ratio) is between about 1:3 to about 3:1.

A large variety of low vapor pressure acids that are compatible with the cell hardware and with the catalysts at both electrodes may be used in accordance with
30 the invention.

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The backing layer is preferably made of carbon. This layer is porous and is used for support and at the same time for making electrical contact between the housing and the catalyst powder, which by itself is connected to the membrane.

The means for circulating an fuel past the anode and for flowing oxygen or
5 air past the cathode include also means for withdrawing carbon dioxide, unused fuel and water from the anode side and for withdrawing unused oxygen and water from the cathode side.

One advantage of the fuel cell according to the invention over current art fuel cells is that it uses a membrane that is easily wet. Thus, there is no need to
10 develop special means for membrane humidification, as is the case in current art fuel cells, as evident, for instance, from US 5,952,119 to Wilson, which states that "one of the primary challenges in attaining optimal performance of polymer electrolyte membrane fuel cell is attaining effective hydration of the ionomeric membrane structure". Wilson suggests solving this problem by applying a
15 hydrophilic wick to wick liquid water to the membrane. As the fuel cell of the present invention does not show wetting difficulties, such a wick is saved, and the cell construction is simplified.

According to one embodiment of the present invention, the fuel cell of the invention is a H_2/O_2 fuel cell, wherein two sets of integrated flow channels are
20 engraved in the cathode chamber or in the anode chamber. In one set of channels of this embodiment reactant gases are flowing, and in the other - the electrolyte is circulating.

According to yet another aspect of the present invention there is provided a method for reconditioning a direct oxidation fuel cell, the method comprises the
25 steps of:

(a) operating the cell at a reversed voltage of 0.6 to 1.3V for a period of time T.

Preferably, the time period T is between 1 to 100 minutes. A longer period T is preferable as the cell ages or as it suffers a higher level of impurities.

30 Preferably, the voltage is between 0.6 and 1.3V.

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The inventors applied this reconditioning procedure 10 times, each time for 1 to 30 minutes, during a 3500 hours operating period of a fuel cell and found an improvement of the cell voltage of 50 to 100mV.

The invention also provides a method for preparing a catalyst layer for use
5 in a fuel cell, said method comprising the steps of forming up to one monolayer of a catalyst on the surface of a nanosize inorganic powder, such monolayer serving as a nucleation site, forming additional one or more catalyst layers on the top of said first monolayer to obtain catalyst particles and subsequently binding the obtained particles to the carbon backing layer and/or to the proton conducting
10 membrane.

According to another aspect of the present invention there is provided a hybrid power source comprising a liquid feed fuel cell according to the invention, a DC to DC converter and a rechargeable battery.

According to another aspect of the present invention there is provided a
15 device for controlling the water return flow from the cathode side to the anode side in a fuel cell, comprising a water or fuel solution level sensor and air or oxygen pressure control unit placed in the cathode compartment, and a fuel cell comprising such a device.

According to another aspect of the present invention there is provided a
20 method for reducing crossover current in a fuel cell having an anode chamber with an anode and a fuel tank for providing said anode with fuel, a cathode chamber with a cathode and means for providing said cathode with oxygen in a given pressure, a solid electrolyte membrane disposed between said cathode and said anode, and a tank for water or fuel solution, an air or oxygen pressure control
25 unit and a sensor for sensing the level fuel solution in said fuel tank and means for controlling said pressure in response to said level of water or fuel, comprising the steps of:

(a) sensing the level of the water or fuel in the water or fuel tank;

(b) controlling the air or oxygen gas pressure in the cathode chamber to

30 increase as the level of water or fuel solution sensed in step (a)

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decreases;

thus reducing the crossover current.

According to another aspect of the present invention there is provided a free direct oxidation fuel cell having a low crossover current density, wherein the fuel solution tank is directly attached to the anode chamber, the fuel concentration is between 1% and 40% (w/w) and the ratio between the tank volume (in ml) and the electrode area, in cm^2 is between 3:1 and 30:1.

According to another aspect of the present invention there is provided an orientation independent direct oxidation fuel cell system having

- 10 (a) an anode chamber with an anode, fuel inlet and gas outlet;
- (b) a cathode chamber with a cathode and oxygen or air inlet;
- (c) an electrolyte membrane disposed between the anode and the cathode;
- and
- (d) a fuel tank connected to the anode chamber,

15 wherein

- i) said fuel tank being divided by a movable barrier into two parts, said first part of the fuel tank being capable of containing fuel or fuel solution and connected to the anode chamber, said second part of the fuel tank holding gas with pressure greater than atmospheric pressure or having a closable gas inlet;

- 20 ii) said gas outlet being closed with a gas permeable hydrophobic matrix;

said barrier being capable of directing fuel or fuel solution from the fuel tank to the anode chamber irrespective of the fuel cell orientation.

25

BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, several embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

5

Fig. 1 shows a schematic representation of a multi-cell fuel system.

Fig. 2 shows an integrated gas - acid solution flow field system used in a hydrogen/oxygen fuel cell.

Fig. 3 shows a graph illustrating polarization curves at different methanol
10 concentrations.

Fig. 4 shows a graph illustrating polarization curves for different acids.

Fig. 5 shows a graph illustrating the effect of additives on polarization curves.

Fig. 6 shows a graph illustrating the relation between the pore size of PCMs
15 and temperature of hot press

Fig. 7 shows a graph illustrating three consecutive polarization curves (3M H_2SO_4 + 1M MeOH at 65°C.).

Fig. 8 shows a schematic representation of a H_2/O_2 fuel cell with integrated gas-acid flow field.

Fig. 9 shows a graph illustrating a polarization curve for a H_2/O_2 fuel cell
20 (25°C, 1psi H_2 and O_2 pressure).

Fig. 10 shows a graph illustrating the polarization curve of a cell operating with a solution of 1M MeOH in 3M sulfuric acid.

Fig. 11 shows a schematic representation of a fuel cell which operates as a
25 primary battery.

Fig. 12 provides a schematic representation of an improved solid feed organic fuel cell having a solid polymeric membrane configured in accordance with a preferred embodiment of the invention.

Fig. 13 is a schematic illustration of an orientation independent hybrid

power source according to one embodiment of the present invention.

DETAILED DESCRIPTION

Several embodiments of the invention will be described and exemplified with reference to the figures.

5 According to one aspect of the present invention there is provided an improved fuel cell. The fuel cell to be improved by the invention includes an anode chamber including an anode and means for providing fuel to the anode, a cathode chamber including a cathode and means for providing oxygen to the cathode, and a solid electrolyte membrane disposed between said cathode and said
10 anode. Such fuel cells and their way of operation are well known in the art. The present invention seeks to improve prior art fuel cells by applying as an electrolyte membrane a proton conducting membrane having pores with a diameter, smaller than 30 nm, said membrane comprising:

- 15 (i) 5% to 60% by volume, preferably 8% to 30% by volume of an electrically nonconductive inorganic powder having a good acid absorption capacity, said powder comprising nanosize particles;
- (ii) 10% to 90% by volume, preferably 30% to 80% by volume of an acid or aqueous acid solution; and
- (iii) 5% to 50% by volume, preferably 12% to 40% by volume of a
20 polymeric binder that is chemically compatible with said acid, oxygen and said fuel.

The anode, the cathode and the solid electrolyte membrane are typically hot pressed so as to form a single structure unit. The fuel used by the cell may be, for example, a pure organic liquid fuel, an aqueous solution of an organic fuel, a
25 water solution comprising an acid and an organic fuel, or a gas. A large variety of low vapor pressure acids that are compatible with the cell hardware and with the catalysts at both electrodes may be used in the acid-fuel solution. Non-limiting examples for such acids are: alkyl sulfonic acids, polyfluoroolefin sulfonic acid, perfluoroolefin sulfonic acid, aryl sulfonic acids, polyfluoroaryl sulfonic acids,

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such as polyfluorobenzen, polyfluorotoluene, or polyfluorostyrene sulfonic acid, perfluoroaryl sulfonic acids, such as perfluorobenzene, perfluorotoluene or perfluorostyrene sulfonic acid, and similar acids where up to 50 % of the hydrogen or fluorine atoms were replaced by chlorine atoms, $\text{CH}_3\text{CH}_2\text{SO}_3\text{H}$, benzyl sulfonic acid, $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$, $\text{HO}_3\text{S}(\text{CF}_2\text{CH}_2)_n\text{SO}_3\text{H}$, $\text{CF}_3(\text{CF}_2\text{CH}_2)_n\text{SO}_3\text{H}$, $\text{HO}_3\text{S}(\text{CF}_2)_n\text{SO}_3\text{H}$ where n is an integer having a value of 0 to 9, NafionTM ionomers, phosphoric acid, sulfuric acid, sulfamic acid and mixtures thereof

To the acid-fuel solution it is possible to add, according to the present invention, a soluble catalyst such as a macrocyclic complex of nickel, cobalt or iron. Such a complex may promote the oxidation of the fuel and/or the reduction of the oxygen. The solid electrolyte membrane is a proton conducting membrane (PCM) having pores with a typical diameter smaller than 30nm, preferably smaller than 3 nm, more preferably smaller than 1.5 nm. The membrane comprises inorganic powder of nanosize particles, an acid or aqueous acid solution, and a polymeric binder. The inorganic powder is electrically nonconductive, it has a good acid absorption capacity, and it constitutes 5% to 60%, preferably 8% to 30%, of the membrane volume. The acid or aqueous acid solution constitutes 10% to 90% , preferably 30% to 80% of the membrane volume. The acid of the membrane 6 is that of the fuel-acid solution. The polymeric binder constitutes 5-50% preferably 12 to 40% of the membrane and is chemically compatible with the acid of the membrane, with oxygen and with the fuel used in the cell.

It is shown in detail hereinbelow, that in comparison to current-art NafionTM membranes, the PCMs used in the fuel cell of the present invention have a better conductivity and lower crossover for methanol or other fuels. It is also shown that the PCMs of the invention have the advantages over the NafionTM PCM in not being affected by heavy metal impurities and in being operable at temperatures higher than 100°C or lower than 0°C. Furthermore, the cost of the PCMs of the invention is lower than that of NafionTM by about two

orders of magnitude, thus lowering the price of the entire fuel cell.

The invention further provides the following improvement in fuel cells:

Improving the efficiency of a fuel cell

5 In this section we describe several techniques for improving the efficiency of fuel cells. These techniques were invented during the investigation of the fuel cell of the invention, however, some of them may also be applied for improving current-art fuel cells.

As known in the art, one of the factors that reduce fuel cells efficiency is
10 fuel crossover, i.e. the undesired permeation of the fuel molecules through the electrolyte membrane to the cathode chamber, thus lowering the operating potential of the fuel cell. The rate of crossover is known to be proportional to the permeability of the fuel through the solid electrolyte membrane and to increase with increasing concentration and temperature.

15 The inventors found that the use of the fuel cell of the invention with pores smaller than 1.5nm is one way to reduce the crossover current. For example, the crossover current density for a NafionTM 117 membrane (that have pores of 3-4nm), in 1M methanol at 60 °C is 140 mA/cm², while that of the PCM used in the present invention (having pore size of less than 1.5nm) is 18.5-25
20 mA/cm², at 65°C and 31.8 mA/cm² at 75°C.

Furthermore, it has been found by the present inventors that the permeability of the solid electrolyte membrane to the liquid fuel can be further reduced with minor effect on the conductivity, by changing the membrane properties such as pore size diameter and pore's neck diameter. Such a change
25 may be achieved by filling these pores with proton conducting materials or by adding salts to the fuel acid solution. Therefore, in a preferred embodiment of the present invention the solid electrolyte membrane has pores that are partially filled with proton conducting materials. Another preferred embodiment of the present invention has a solid electrolyte membrane which further comprises salts. Other
30 PCMs, such as NafionTM may also benefit from partially filling their pores with

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proton conductive materials. In addition, it has been found that fuel crossover may be further reduced by filling the pores of the PCM with a Na_2SiO_3 solution and hydrolyzing the silicate in sulfuric acid to form in the pores nano particles of hydrated silica or silicic acid. Alternatively, this effect can also be achieved by
5 filling the pores with a polyhetroacid such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and preferably hot pressing the PCM so as to reduce the size of the pore's neck and to lock the acid in the pores.

Fuel crossover may also be reduced by lowering the concentration of the fuel or by choosing a fuel having a molecular size larger than that of methanol,
10 thus having a smaller diffusion coefficient. Examples of such known fuels are, methylformat, ethylformat, dimethoxymethane, trimethoxymethane and trioxane.

It has been found that the crossover of methanol in the fuel cell of the invention may be further reduced, by adding to the acidic fuel solution salts such
15 as soluble organic sulfonates, for example: potassium benzene sulfonate, or the sulfates of zinc, aluminum, potassium, sodium, cobalt, manganese, nickel, cesium, or magnesium preferably in the form of hydrates. Typical amounts of salts to be added are such as to provide an acid to salt molar ratio of between 1:10 and 10:1. Preferable salts are those wherein both cation and anion are not
20 susceptible to electrochemical reactions, such as sulfates of alkaly metals, alkaline earth metals, zinc and aluminum. Other considerations in selecting a salt to be used according to this aspect of the present invention is that preferable salts should be compatible with oxygen, with the catalysts and with the fuel and should not form electronically conductive residues when dry. They preferably have high
25 dehydration temperatures, indicating a strong bonding of water. Examples for such hydrates and their decomposition temperatures (in brackets) are $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (280°C), $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (86°C), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (150°C), NiSO_4 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (96.8°C), $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ (280°C). Alkali sulfates such as Cs_2SO_4 and Na_2SO_4 have high solubility and reduce the water vapor pressure. Thus,
30 enabling the use of the fuel cell at low pressures above 100°C. Ammonium

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sulfate has high solubility but it may decompose slowly, therefore, it may also be useful at low temperatures. Another advantage in adding salts to the fuel solution is that some of them may function at elevated temperatures as molten hydrates and reduce the water vapor pressure, thus allowing for the operation of the fuel cell at temperatures higher than 100°C. Operating at such elevated temperatures may be advantageous, since at these temperatures steam may be produced to allow co-generation of heat and electricity, and to lead to a higher energy conversion efficiency. In addition, at high temperature of operation the fuel cell can tolerate higher concentrations of CO and smaller amounts of expensive catalyst is needed. Notably, apart of the salts added to the fuels, it is also the acid contained in the fuel solution which helps fuel cells which make use of acidic fuel solution to operate in temperatures wherein water is not liquid. For instance, a 27% H₂SO₄ solution freezes at -27°C.

15

Sensitivity to heavy metals

As mentioned above, the PCM used in the fuel cells of the invention is not affected by heavy metal impurities, while Nafion is very sensitive to heavy metals impurities. For example, 500 ppm chromium reduced the conductivity of a Nafion based membrane by a factor of eight from 0.1 S/cm to 0.013 S/cm (Warthesen and Shores Extended Abstract Vol. 33rd). The same concentration of iron, which has similar effect on conductivity as chromium, did not significantly affect the conductivity of the PCM used in the invention. The tested PCM consisted of (V/V) 24% PVDF (polyvinyliden fluoride) as a binder, 16% SiO₂ as an inorganic nanopowder and 60% 3M sulfuric acid. The conductivity measured without iron impurities was 0.18 S/cm, while that measured in the presence of 500 ppm iron sulfate was 0.17 S/cm. This feature of the PCM used in the invention is very important and unique as it enables the use of catalysts consisting

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of non noble metals or Pt alloys with non-noble metals (M) such as Fe, Ni or Co. It was found that Pt-M alloys are much better catalysts for oxygen reduction, and the preferred ratio Pt-M is between 1:3 to 3:1. These results also make possible the use of metals like super alloys and low corrosion stainless steel alloys for the fuel cell hardware and for peripheral subsystems with smaller risk of affecting the conductivity of the membrane.

Preparation of a catalyst layer

The catalyst used for the air (oxygen) cathode is commonly nano particles (preferably 2-5 nm) of Pt or Pt alloys where the one used at the methanol anode is a Pt - Ru alloy of nano size (preferably 5 - 10 nm) particles. However, in order to save the cost of expensive noble metals, it is possible to use non noble metal based alloys such as for example Ni, Fe or Co and coat them with the required noble metal catalyst by common electrochemical or chemical processes. The thickness of such catalyst layer may be between less than one monolayer to 20 monolayers.

After long operation periods, the bond between the catalyst particles and the supporting carbon matrix is lost leading to the degradation of the fuel cell. In view of that it is proposed in the present invention to bind the nano size catalyst to a nano size ceramic powder and subsequently bind the obtained particles to the carbon backing layer and to the PCM. A good way to perform this is to use the well-known commercially available electroless process. According to this process, up to one monolayer of a catalyst salt (like PtCl_4 , RuCl_3 , etc.) is adsorbed in the first step on nano size hydrated silica powder by immersing the powder in a solution containing a predetermined amount of the catalyst salt. Then, in the second step, a proper amount of a reducing agent like formaldehyde, methanol, formic acid or hypophosphite is added at a suitable pH and temperature to form up to one monolayer of catalyst bonded to the surface of the ceramic powder. This monolayer provides nucleation sites for further deposition. Next, one or several catalyst salts and more reducing agents are added to form the final size of the catalyst particles.

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For a methanol anode it is preferred to form either a Pt-Ru alloy catalyst layer or to form two consecutive layers of Pt on Ru or Ru on Pt with atomic ratio of 1:10 to 10 : 1. Other elements, like Sn, Os, Ni can be added to the catalyst layer to further improve the kinetics of fuel oxidation. In the same way catalyst layers consisting of
5 Pt or Pt nano size alloys with Co, Ni, Fe, or Ag can be prepared for the oxygen cathode.

The present invention also provides an improvement in hydrogen/oxygen fuel cells, which use a PCM according to WO 99/44245, having acid solution as
10 its electrolyte, instead of current art Nafion™ based electrolyte membranes. According to this improvement, a new integrated gas – acid solution flow system (shown in Fig. 2) was designed in order to prevent changes in electrolyte concentration during fuel cell operation. In this system two integrated sets of flow channels 100 and 110 are engraved into the cell housing, as opposed to one set of
15 flow channels generally employed in fuel cells. In one set of channels reactant hydrogen gas is flowing and in the second set an aqueous acid solution (i.e. electrolyte) is circulating. The electrolyte pressure in the integrated flow field system can be equal, higher or lower than the reactant gas pressure. If it is desired to prevent from reactant gas to penetrate into the flow channels of the electrolyte,
20 a higher electrolyte pressure will be used. At the contrary, if it is desired to prevent the electrolyte from penetrating into the gas flow channels, a lower electrolyte pressure will be used. If both effects are equally undesired, equal pressures of electrolyte and reactant gas will be used.

When preparing the integrated flow field system in the housing of the fuel
25 cell, the maximum allowed distance between adjacent electrolyte and gas flow channels would usually be a factor of the membrane capillary forces. The ratio of electrolyte flow channels to gas flow channels will usually be determined by individual system optimization and by comparing the need to supply electrolyte versus the need to supply reactant gasses.

30 In Figure 2 an integrated flow system is shown schematically. Through the

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channel 100 a reactant gas, i.e. hydrogen, (entrance at 1A and exit at 1B) flows, while through the channel 110 the electrolyte (entrance at 2A and exit at 2B) is circulated. In the flow system shown schematically in Fig. 2 the ratio of electrolyte flow channels to gas flow channels is 1: 2 and the maximum distance
5 between adjacent electrolyte flow channel and gas channel is 8 mm.

The integrated flow field system of the invention can be formed either on the anode side or on the cathode side or on both sides.

The integrated flow field system can also be used as a part of the temperature control system, or as a part of the water removal system (by
10 controlling water vapor pressure via temperature gradient).

Hybrid power sources

Direct methanol fuel cell (DMFC) and liquid feed fuel cells (LFFC) are low power sources. However, devices like cellular telephones, computers and
15 small electric vehicles need high power for short times. For these and for similar applications it is possible to combine a fuel cell according to the invention with a small high power rechargeable battery, which supplies the high power when required. Such a combination is advantageous over current art hybrid power source, *inter alia* thanks to the small crossover current. Today DC to DC
20 converters can start working from 0.7V. As a result it is possible to combine as few as two or three fuel cells (in a series combination) through a DC to DC converter to a battery. If the crossover current density is small enough, say 15 preferably 5mA/cm² or less, such a hybrid power source need not be fueled very often. Therefore, this hybrid power source is preferably with a fuel cell of low
25 crossover current such as the fuel cell of the invention. The fuel cell charges the battery and supplies the low power demand while the high power battery supplies the heavy loads. This small number of required fuel cells enables the use of a flat and thin fuel cell system .

For example, to power a cellular phone it is possible to use a hybrid power
30 source built of two thin methanol fuel cells, connected in a series combination, a

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DC to DC converter and a small high power lithium ion cell.

Water balance mechanism

In any fuel cell based on a proton conducting membrane the protons that
5 cross through the proton conducting membrane carry with them about three water
molecules per proton. In a DMFC six protons move through the membrane for
each methanol molecule. It means that 18 water molecules are carried out by the
protons per each methanol molecule that was oxidized.

This phenomenon causes a significant loss of water. Usually, in order to
10 minimize water loss, the water from the exhaust of the fuel cell are collected and
recycled. A new way to minimize water loss is suggested here. It was found that
the application of excess pressure in the cathode compartment causes a decrease
in the methanol crossover. Each 0.1 atmospheres excess gas pressure causes a
decrease of about 10 % in the crossover current (for example, at 1M methanol
15 and at 60 degree C it decreases by 7 mA/cm², from 70 mA/cm² to 63 mA/cm²).
This is explained by hydraulic stream of the fuel solution from the cathode side to
the anode side. As the water methanol ratio is about 53:1, the back stream of
water by this effect is equivalent to 7x53 or 371 mA/cm², or to a water flux of
0.371x 10⁻⁶ moles per sec.cm². This effect can be utilized as water return
20 mechanism in any fuel cell comprising a proton conducting membrane. At steady
state the protons current equals the external load electronic current and the water
flux carried out by the protons is three times larger. As a result at a load of
100mA/cm² the water flux is equivalent to 300 mA/cm² and an excess pressure of
0.1 atmospheres may be enough to return the water back from the cathode side to
25 the anode side. A water (or fuel solution) level sensor can be installed in the
water (or fuel solution) tank and the air or oxygen pressure at the cathode
compartment will be controlled to keep this water (or fuel solution) level
constant.

Such a device was found by the inventors to reduce the crossover current.
30 It is therefore provided by the present invention a device comprising a solution

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level sensor and a gas pressure control unit; said gas pressure control unit being capable to control the gas pressure in response to the solution level as sensed by the sensor. In particular the invention provides a fuel cell having an anode chamber with an anode and means for providing the anode with fuel, a cathode
5 chamber with a cathode and means for providing the cathode with oxygen in a given pressure, a tank for water or fuel solution, an air or oxygen pressure control unit and a sensor for sensing the level of the water or fuel solution in said tank and means for controlling said pressure in response to said level of water or fuel, and a method for reducing crossover current in such a fuel cell, comprising the
10 steps of:

(a) sensing the level of the water or fuel solution in the water or fuel solution tank;

(b) controlling the air or oxygen gas pressure in the cathode chamber to increase as the level of water or fuel solution sensed in step (a)
15 decreases ;

thus reducing the crossover current.

Pump free DOFC

The present invention also provides, according to another of its aspects, for a direct oxidation fuel cell, which has no pumps. The pump and valves of current art fuel cells, which are not needed any more according to this aspect of the invention, are used to deliver fuel from a fuel reservoir to the anode chamber. This delivery is needed because current art crossover levels are such that necessitate large fuel reservoirs (due to large quantities of fuels that are spent on crossover). The present invention thus provides for a pump free direct oxidation fuel cell, wherein the fuel tank is directly attached to the back side of the anode (the opposite side to the PCM), as, for instance illustrated in Example 5, bellow. In order for such a cell to be of practical use, it should have a low crossover current, typically $15\text{mA}/\text{cm}^2$ or less, preferably $5\text{mA}/\text{cm}^2$ or less, more preferably $2\text{mA}/\text{cm}^2$ or less. Otherwise, the fuel tank should be non-practically large, or the lifetime of the cell becomes inconceivably short. The required low crossover current may be achieved by applying a PCM of the kind described in WO99/44245, or its improvement suggested above.

At room temperature, the crossover current density measured in a fuel cell according to this aspect of the invention provided with 3% methanol, was less than $5\text{mA}/\text{cm}^2$. A 25cm^2 cell can supply between 300 to 600mA and has a crossover of 125mA (under no load conditions). When a tank of 300ml acidic fuel solution is attached to such a pump free DOFC it contains (3% X 300ml =) 9gr methanol, which may produce 45Ah. These 45Ah may be consumed by the crossover for 720 hours. Under these conditions a few grams of methanol should be added to the fuel tank once a week, making it a very convenient power source.

Typically, two or three such cells are used in combination with a DC to DC converter to give a hybrid power source as described above. Such a hybrid power source may be conveniently used as a battery charger for cellular phones and other small appliances. For a practical, pump free DOFC having a PCM with crossover current density of between $1.5\text{mA}/\text{cm}^2$ to $15\text{mA}/\text{cm}^2$. The ratio between the fuel

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tank volume (in ml) and the electrode area (in cm^2) should preferably be between 1:3 to 1:230.

Orientation independent fuel cell

5 When a fuel cell is used in a portable device, such as cellular phone, it should be designed to be orientation independent, so that fuel reaches the cell from the fuel tank irrespective of the cell orientation. Thus, the present invention provides, according to another of its aspects, an orientation independent direct oxidation fuel cell, having an anode chamber with an anode, fuel inlet and gas
10 outlet, said gas outlet being closed with a gas permeable hydrophobic matrix; a cathode chamber with a cathode and oxygen inlet; an electrolyte membrane disposed between the anode and the cathode; and a fuel tank connected to the anode chamber, wherein said fuel tank being divided by a movable barrier into two parts and; said first part of the fuel tank being capable of containing fuel and is
15 connected to the anode chamber, said second part of the fuel tank having a closable gas inlet, and said barrier being capable of directing fuel from the fuel tank to the anode chamber irrespective of the fuel cell orientation.

Usually, said second part of the fuel tank is full with gas at a pressure that is higher than atmospheric pressure so that the gas is capable of pushing the barrier to
20 direct fuel out of the fuel tank into the anode chamber. Alternatively, the second part of the fuel tank is full only with atmospheric air until operation, when it is filled through the gas inlet with CO_2 , evolving from the oxidation of the fuel at the anode chamber.

Such an orientation independent fuel cell is also pump free and require
25 only a small number of valves.

The invention will be further described in more detail in the following non-limiting examples.

Example 1

30 a) First fuel cell configuration

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A fuel cell housing was fabricated from synthetic graphite plates purchased from Globetech Inc., in which a flow field was engraved.

The anode was formed using a platinum-ruthenium ink that was spread on a carbon fiber sheet commercially available from Toray TM paper. Several types
5 of inks were prepared, as follows:

1. Type A was prepared by mixing 600 mg of 60% Pt:Ru on Vulcan XC-72 (purchased from E-Tek Inc), 60 mg Kynar 2801 PVDF, 0.26 ml propylene carbonate (PC) and about 1.5 ml of cyclopentanone;
2. Type B was prepared by mixing 600 mg of 20% Pt/ 10% Ru/
10 Vulcan C-72 (purchased from ElectroChem, Inc), 60 mg Kynar 2801 PVDF, 0.38 ml propylene carbonate (PC) and about 1.5 ml of cyclopentanone;
3. Type C was prepared by mixing 600 mg of 20% Pt/ 10% Ru/ Vulcan XC-72 (purchased from ElectroChem, Inc), 60 mg Kynar 2801
15 PVDF, 60 mg Aerosil 130 (purchased from Degussa AG), 0.42 ml propylene carbonate (PC) and about 1.5 ml of cyclopentanone.

The inks were magnetically stirred over night and then 3-4 layers were painted by a paint brush on the Toray TM paper.

- The cathode was formed by painting a Pt ink on teflonated TorayTM paper.
20 The ink was prepared by mixing 600 mg of 80% Platinum on Vulcan XC-72 (purchased from E-Tek, Inc), 60 mg Kynar 2801 PVDF, 0.17 ml propylene carbonate (PC) and about 1.5 ml of cyclopentanone.

The PCM was manufactured by mixing 14.87 g of powdered Kynar PVDF 2801-00 and 12.88 gr of high surface area, 16 nm particle size silicon dioxide,
25 >99.8% (Degussa), with 150 ml of cyclopentanone and 21 ml of propylene carbonate (PC). Part of the viscous mixture obtained, was poured onto K control coatter (R K Print, Coat Instruments) and a film was made by using doctor blade method. The film was allowed to dry at room temperature for several hours and an elastic, strong, transparent film was obtained.

30 The film was washed by using double distilled water in order to remove

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the PC. Following the washing, a catalyst layer (Pt:Ru or Pt, depending on the electrode) was painted on the outer side of the membrane. Following this step, the film was immersed in 30% wt H₂SO₄ for 1.5 hours at 60°C or over night at room temperature. After cooling the film was placed between the Toray papers, a polypropylene sealing was inserted and the cell was assembled. The impedance of a six cm² cell thus obtained was measured by using AC impedance spectroscopy Solartron model SF 1260 and was found to be smaller than 0.1 ohms (at 25° ± 3°C).

Other cells were manufactured by hot pressing a PCM sandwiched between two Toray TM papers coated by proper catalysts, at temperatures between 70 and 130 °C.

During fuel cell operation an aqueous solution containing acid and 0.4-2 mole/liter methanol was circulated past the anode (with the use of a peristaltic pump type) at different flow rates, from 1 to 20 ml/min. Fig. 3 shows polarization curves for different methanol concentrations.

The following acids and acid concentrations were tested: 1-3 mole/liter H₂SO₄, 1:3-1:6 mole ratio CF₃SO₃H:H₂O and 40 % (w/w) aqueous PWA (i.e. H₃PW₁₂O₄₀) solution. Fig.4 shows polarization curves for two acidic, aqueous solutions, each containing 1. 3M H₂SO₄ + 1M methanol and 2. 1:6 (V/V) CF₃SO₃H:H₂O + 2M methanol.

In the same manner additional fuel cells were built and other fuels such as formaldehyde, formic acid, methylformat, ethylformat, oxalic acid, glycerol, ethylene glycole and dimethyloxalat were tested.

b) Second fuel cell configuration

A second cell configuration was manufactured by painting the anode side flow field and both sides of the anode Toray TM paper with Pt:Ru ink. This modification was made in order to increase the catalyst content per square cm.

Example 2

The crossover was measured by two test methods:

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1. Using the regular configuration of the fuel cell but using nitrogen instead of oxygen at the anode and methanol in 3M H₂SO₄ at the cathode. The current (at 1V) measured is a product of the oxidation of the methanol that penetrated through the PCM from the cathode to the anode side.

- 5 2. The same as in Method 1 above but both electrodes were painted with Pt-Ru ink and the crossover current was calculated in the same way as in 1.

The crossover currents are summarized in Table 1. The crossover of 1 mole/liter methanol was measured at 50,65 and 75 °C.

- 10 (i) Table 1: Crossover current densities at different temperatures and test methods (1 M methanol and 3 M sulfuric acid in H₂O), and a PCM with and 24 % PVDF, 16% SiO₂ (w/w), hot pressed at 70 °C. The PCM thickness was 300 micron and it was 60% porous.

Temperature [°C]	Test method 1		Test method 2	
	Current density [mA/cm ²]	Cell Voltage [v]	Current density [mA/cm ²]	Cell Voltage [v]
50	26	1	13	1
65			18.5	1
75			31.8	1

15

The measured crossover currents (at 1V) for the second cell configuration (with the Pt:Ru ink on the flow field) was 25.5 mA/cm² for 1 mole/liter methanol at 65°C and 58.3 mA/cm² for 2 mole/liter methanol at 65°C.

- 20 The crossover current density for 0.1M oxalic acid was measured at 65°C according to Method 1 and was found to be 0.3 mA/cm². The crossover current density for 0.1M dimethyl oxalate was measured at 65°C according to Method 1 and was found to be 6 mA/cm².

In order to reduce crossover of methanol through the PCM, the PCM was hot pressed at different temperatures between 70 and 130°C. The hot press was

made in hydraulic press at about 40 Atmospheres for 30 - 250 seconds. As can be seen in Fig. 6 the pore size distribution, that was measured with Quantachrome NOVA 2200 Surface Area Analyzer, changed significantly upon the hot press. It was found that for an unpressed PCM, a significant volume of the material tested had pores dimension of less than 3nm, while for a PCM that was subjected to hot pressing, a significant volume of the material tested had pores dimension of less than 1.5 nm. These nanosize pores have good retention capability for the acid and are small enough to reduce the methanol crossover.

The effect of additives on the crossover is showed in Table 2 and in the polarization curves presented in Fig. 5. The PCM used consisted of (V/V) 24 % PVDF, 16 % SiO₂ hot pressed at 70 °C, 60 % 3 M sulfuric acid with the added metal sulfates. PCM thickness was 300 micron.

Table 2: Additive's influence on methanol crossover current, 1M methanol, 65 °C.

Additive	Salt Concentration [M]	Crossover current density [mA/cm ²]
MgSO ₄	2	10
ZnSO ₄	1	20.8
ZnSO ₄	2	11.2
Al ₂ (SO ₄) ₃	0.5	13.5
Control	0	25.5

15

Example 3

In order to improve performance, another methanol fuel cell was manufactured with the use of pure metal catalysts, instead of carbon supported catalysts. A cathodic catalyst ink was prepared by the following process:

A nano powder Pt (Pt black, purchased from "Johnson Matthey"), TeflonTM emulsion and NafionTM 5% solution were combined in the following weight

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proportions: 60%Pt, 25% Teflon emulsion and 15% Nafion. First the Pt powder and the Teflon emulsion were mixed by sonication for 15 minutes. After two sonication periods, the ink obtained was placed on a magnetic stirrer for at least one night.

5 An anodic catalyst ink was prepared by the following process: A Pt:Ru nano powder (Pt:Ru black 50% purchased from "Johnson Matthey") and PVDF were mixed in the following weight proportions: 91% catalyst powder and 9% PVDF. Propylene carbonate was added in an amount equal to 30-70% of the catalyst volume, then cyclopentanone was added and the ink obtained was stirred
10 for at least one night.

Preparation of the electrodes: the cathode catalyst ink was applied on teflonated TorayTM carbon fiber paper, to form 4 mg Pt/cm². The ink (in the form of a paste) was spread in layers, allowing each layer to dry for about one hour, before the next layer was applied. This operation was repeated until the desired
15 amount of catalyst was obtained. In the same way, the anode catalyst ink was applied on unteflonated TorayTM carbon fiber paper, until 5-10 mg catalyst/cm² was obtained. Both electrodes were washed with 3M sulfuric acid and then with water.

The cathode was hot pressed under a pressure of 10-70 Kg/cm², at a
20 temperature of 85-130°C to one side of a PCM with a thickness of 100-300 µm. The anode was placed on the other side of the PCM, parallel to the cathode and the complete cell was assembled.

Fig. 7 illustrates three consecutive polarization curves for this kind of fuel cell, under the following conditions: a solution of 1M MeOH and 3M H₂SO₄ was
25 circulated through the anode at a rate of 9ml/min. Oxygen was circulated past the cathode at a pressure of 0.25 atm. over the atmospheric pressure. The cell temperature was 65°C. A 300 micron thick PCM consisting of (V/V) 16% nanosize powder of SiO₂, 24% PVDF and 60% pore volume, of 1.5 nm typical diameter. The cell demonstrated over 100 hours of stable operation at 0.4V. After
30 100 hours of operation the current change was less than 3%.

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Other cells were built according to the same procedure described above, but using another cathode ink. This cathode ink consisted of (weight %) 0-5% nanosize SiO_2 , 20-40 % Teflon and 40-80 % nanosize Pt powder. Fig. 10 illustrates the polarization curves of these cells, operating with a solution of 1M MeOH in 3M sulfuric acid.

Measurements of fuel crossover were carried out at several temperatures by feeding nitrogen instead of oxygen into the cathode compartment (at ambient pressure) and feeding organic fuel-acid solution into the anode compartment. Cell voltage was reversed; hydrogen was evolved at the fuel electrode while fuel that crossed over to the cathode side was oxidized. The current that flows at 1V was found to be the limiting current for fuel oxidation.

Example 4: H_2/O_2 fuel cell

We engraved an Integrated Flow Field System into a graphite housing. The system is schematically described in Fig. 2. In this system the ratio of the electrolyte flow channels to gas flow channels is 1 : 2 and the maximum distance between adjacent electrolyte flow channels is 8 mm. We have fabricated a fuel cell system with an Integrated Flow Field System at the anode side. We then attached the fuel cell to gas providing systems that combined with an electrolyte circulating system. This system is built in such a way that the hydrogen and the electrolyte pressures at the Integrated Flow Field System are equal. The gas/electrolyte providing system is shown schematically in Fig 8.

Fig. 8 illustrates a H_2/O_2 fuel cell 200 having a housing 210, an anode 220, a cathode 230 and a solid PCM 240. A hydrogen gas providing system 250 provides hydrogen to the fuel cell. An oxygen providing system 260 supplies oxygen either directly (as shown in Figure 8) or via the electrolyte tank 270 in order to achieve an equalization in pressures. The cell further comprises an oxygen purge system 280, an electrolyte pump 290 and a hydrogen purge system 300. The pump we used was a peristaltic pump and the electrolyte was 1.5 M sulfuric acid.

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Figure 9 shows a polarization curve for this fuel cell, at 1 PSI (over atmospheric pressure) hydrogen and oxygen pressure, at room temperature (about 25 °C). The electrolyte was circulated at 9 ml/min.

5 Example 5

The low fuel crossover enables the use of the fuel cell of the invention as a replacement for a primary battery. In this case, a fuel-acid solution is not circulated but is stored in the anode side (compartment) in a porous carbon matrix. The air inlet ports may be closed, for example, by adhesive tape when this
10 fuel cell is not in use.

Figure 11 illustrates schematically this kind of fuel cell, having 0.6mm thick Hastelloy C-276TM end plates 300, porous non-woven carbon felt (or matrix) RVC 1000TM (Carbone Lorraine) 310 which on one side serve as an air flow field and on the second side as storage cell for the fuel solution; TorayTM
15 paper 320 and a Teflonated TorayTM paper 325 as backing layers, a PCM 330, air inlet ports 340, a fuel solution filling port 350, TeflonTM sealing rings 360, plastic envelopes made of shrinkable tube 370 for holding and sealing the whole assembly. On the cathode side of the PCM, 5 mg nanosize Pt catalyst (purchased from Johnson Matthey) was spread following the procedure described in Example
20 3, on the teflonated Toray paper 325 to form a catalyst layer 380 while on the anode side, 5 mg of nanosize Pt-Ru 1:1 (atomic ratio) catalyst (Johnson Matthey) was spread following the procedure described in Example 3, on TorayTM paper 320 to form a catalyst layer 390. Both Toray papers (after applying the catalysts) were hot pressed to the PCM at 100°C and under a pressure of 40 kg./cm² for
25 200 sec. After cell assembly, a solution containing 1 M H₂SO₄ and 0.5M methanol was inserted through the fuel filling port 350 (closed by adhesive tape), and the cell was discharged. The open circuit voltage of the cell was 0.5V, and it delivered 1mA/cm² for a few minutes.

In another experiment, a cell was assembled having a fuel tank of
30 thickness 4mm, located at the back side of the anode, and a PCM made of 10%

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silica, 30% PVDF and the balance voids, later filled with 3M H₂SO₄. After cell assembly a solution containing 3M H₂SO₄ and 1M methanol was inserted through the fuel filling port 350 (closed by adhesive tape), and the cell was discharged. The open circuit voltage of the cell was 0.65V and it delivered 1mA/cm² for a few hours. The crossover current density was 2mA/cm². This low crossover value allows the use of fuel solutions with concentrations of 1% to 40%, compared with 3% to 6% that are feasible with current art cells.

Example 6: An orientation independent DOFC

Figure 13 illustrates an orientation independent direct oxidation fuel cell system that makes use of several aspects of the present invention. The system 1000 comprises a fuel cell 1100, having an anode chamber 1110 with an anode 1112, a fuel inlet 1114 and a gas outlet 1116, a cathode chamber 1120 with a cathode 1122 and air inlet holes 1124, an electrolyte membrane 1200, preferably according to WO99/44245 and/or this invention, disposed between the anode 1112 and the cathode 1122, and a fuel tank 1300, which preferably is disposable, connected to the anode chamber 1110 through a (liquid) pipe line 1160 and a valve 1162. The fuel tank 1300 is divided by a movable barrier 1310, into two parts: a first part 1312, which contains the fuel (either pure or in solution) and is connected to the anode chamber 1120, and a second part 1314, which optionally has a gas inlet 1316, by which gas may enter the second part 1314 to create there gas pressure of over one atmosphere. Alternatively, the gas pressure is provided by pressed gas stored permanently in the second part 1314. The barrier 1310 may be of any kind known in the art, such as a piston or a bladder. It is capable of directing fuel from the fuel tank 1300 to the anode chamber 1110 through the pipeline 1160 and valve 1162 irrespective of the orientation of the fuel cell system 1000. The gas outlet 1116 is closed with a gas permeable hydrophobic closure (not shown). The anode chamber 1110 and optionally the fuel tank 1300 are further equipped with fuel concentration sensors, 1111 and optionally 1320. The fuel concentration sensors 1111 and 1320 are connected to the controller 2000, which is capable of ordering

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streaming fuel from the fuel tank 1300 to the anode chamber 1110 through pipe line 1160 and valve 1162 in response to a fuel concentration that is under a predetermined value. In such occasions, the valve 1319, which is usually open to allow CO₂ escape into the atmosphere, should be closed.

5 A DC to DC converter 1600 is connected to the fuel cell 1100 and possibly to one or more other fuel cells (not shown) connected in series with the fuel cell 1100 and the DC to DC converter 1600. Thus, the system is actually a hybrid power source in accordance with the invention, capable of charging a battery, such as the battery 1700 or supplying power to a portable appliance 1800.

10 In the embodiment of Fig. 13, the second part of the fuel tank 1314 is full only with atmospheric air until operation, when it is filled through the gas inlet 1316 with CO₂, evolving from the oxidation of the fuel at the anode chamber 1110. The CO₂ is brought from the anode chamber 1110 by pipeline 1150 and valve 1318 to the second part of the fuel tank 1114.

15 The orientation independent fuel cell of Fig. 13 is preferably further equipped with a (preferably disposable) water tank 1500, which construction is similar to that of the fuel tank 1300. The water tank is needed in practice only in dry and hot environments, where water loss due to evaporation may require adding water to the system, or when pure fuel (and not a fuel solution) is used.

20 Otherwise the fuel tank contains enough water for both the electrochemical reaction and the water loss due to evaporation.

CLAIMS

1. A fuel cell comprising an anode side including an anode and means for providing fuel to the anode, a cathode side including a cathode and means for providing oxygen to the cathode, and a solid electrolyte membrane disposed
5 between said cathode and said anode, wherein said solid electrolyte membrane is a proton conducting membrane having pores with a diameter, which is smaller than 30nm, said membrane comprising:

- (i) 5% to 60% by volume, preferably 8% to 30% by volume of an electrically nonconductive inorganic powder having a good acid
10 absorption capacity, said powder comprising nanosize particles;
- (ii) 10% to 90% by volume, preferably 30% to 80% by volume of an acid or aqueous acid solution; and
- (2) (iii) 5% to 50% by volume, preferably 12% to 40% by
15 volume of a polymeric binder that is chemically compatible with said acid, oxygen and said fuel.

2. A fuel cell according to claim 1, wherein said polymeric binder in said proton conducting membrane is selected from the group consisting of polyvinyliden fluoride, poly(vinylidenefluoride)hexafluoropropylene, poly(tetrafluoroethylene), poly(methyl methacrylate), polysulfone amide, poly(acrylamide),
20 poly(vinylchloride), acrylonitrile, poly(vinylfluoride), Kel FTM and any combinations thereof.

3. A fuel cell according to claim 1 or 2, wherein said inorganic powder in said proton conducting membrane is selected from the group consisting of SiO₂, ZrO₂, B₂O₃, TiO₂, Al₂O₃, hydroxides and oxy- hydroxides of Ti, Al, B and Zr, and any
25 combinations thereof.

4. A fuel cell according to any one of claims 1 to 3, wherein said acid in said proton conducting membrane is selected from the group consisting of alkyl sulfonic acid, aryl sulfonic acid, polyfluoroolefin sulfonic acid, perfluoroolefin sulfonic acid, polyfluoroaryl sulfonic acids such as polyfluorobenzen,
30 polyfluorotoluene, or polyfluorostyrene sulfonic acid, perfluoroaryl sulfonic acids

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such as perfluorobenzene, perfluorotoluene or perfluorostyrene sulfuric acid, similar acids where up to 50 % of the hydrogen or fluorine atoms were replaced by chlorine atoms, $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$, $\text{HO}_3\text{S}(\text{CF}_2\text{CH}_2)_n\text{SO}_3\text{H}$, $\text{CF}_3(\text{CF}_2\text{CH}_2)_n\text{SO}_3\text{H}$, $\text{HO}_3\text{S}(\text{CF}_2)_n\text{SO}_3\text{H}$ where n is an integer having a value of 0 to 9, preferably 0 to 5, NafionTM ionomers, sulfuric acid, sulfamic acid, phosphoric acid and mixtures thereof.

5 5. A fuel cell according to any one of claims 1 to 4, wherein said proton conducting membrane has typical pores diameter smaller than 3 nm.

6. A fuel cell according to claim 5, wherein said proton conducting membrane
10 has typical pores diameter smaller than 1.5 nm.

7. The fuel cell of claim 1, wherein said proton conducting membrane further comprises in the pores thereof nanoparticles of hydrated silica or silicic acid.

8. A fuel cell according to any one of claims 1 to 7 wherein said proton conducting membrane further comprises in the pores thereof a polyheteroacid.

15 9. A fuel cell according to claim 8, wherein said polyheteroacid is selected from $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$.

10. A fuel cell according to any one of claims 1 to 9, wherein said aqueous acidic solution further comprises salts selected from ZnSO_4 , $\text{Al}_2(\text{SO}_4)_3$, MgSO_4 , NiSO_4 , CoSO_4 , MnSO_4 , Na_2SO_4 , K_2SO_4 , Cs_2SO_4 , where the salt to acid molar
20 ratio is between 1:10 and 10:1, or polyheteroacids selected from $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 40\text{H}_2\text{O}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$, provided that said salts or polyheteroacids do not induce precipitation of solids during the operation of said fuel cell.

11. A fuel cell according to any one of claims 1 to 10 wherein said proton
25 conducting membrane is hot pressed during its manufacture in order to reduce the pore size.

12. A fuel cell according to any one of claims 1 to 11, wherein the anode, the cathode and the proton conducting membrane are hot pressed at a temperature of between about 70°C and 130°C and a pressure of 10 to 70 kg/cm^2 to form a
30 single structure unit.

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13. A fuel cell according to any one of claims 1 to 8, wherein said acid in said proton conducting membrane is a sulfonic acid chemically bonded to the inorganic powder comprised in said proton conducting membrane, directly or through an organic segment R selected from $-(CH_2)_n-$, $-(CF_2)_n-$, $-(CF_2CH_2)_m-$,
5 where n is an integer from 1 to 10, preferably from 1 to 5 and m is an integer from 1 to 5, preferably 1 to 3, perfluoroaryl, polyfluoroaryl, perfluorostyrene, polyfluorostyrene and similar segments where up to 50 % of the hydrogen or fluoro atoms were replaced by chlorine atoms.
14. A fuel cell according to any one of claims 1 to 12, wherein said fuel is
10 hydrogen and two sets of integrated flow channels are engraved in the cathode side of the housing or in the anode side of the housing, in one set of channels reactant gases are flowing and in the other one the electrolyte is circulating.
15. A fuel cell according to claim 14, wherein the ratio of electrolyte flow channels to gas flow channels is between 1: 5 to 1:1 and the distance between
15 adjacent electrolyte and gas flow channels is between about 4 to about 20 mm.
16. A primary battery comprising a fuel cell as defined in any one of claims 1 to 13, wherein the fuel is in the form of an aqueous solution and it is stored in the anode side of the fuel cell.
17. A primary battery according to claim 16, wherein said means for providing
20 a fuel to the anode and said means for providing oxygen to the cathode comprise means for closure.
18. A method for preparing a catalyst layer for use in a fuel cell, said method comprising the steps of forming up to one monolayer of a catalyst on the surface of a nanosize inorganic powder, such monolayer serving as a nucleation site,
25 forming additional one or more catalyst layers on the top of said first monolayer to obtain catalyst particles and subsequently binding the obtained particles to the carbon backing layer and/or to the proton conducting membrane.
19. A method according to claim 18 wherein the catalyst comprises nanoparticles of Pt or Pt based alloy with up to 90% non noble metals.

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20. A method according to claim 19 wherein said non noble metals are selected from Co, Ni, Fe, Ag, and combinations thereof.
21. A method according to claim 18 wherein said nanosize inorganic powder is a nanosize SiO_2 , TiO_2 , Al_2O_3 , Ag, or nickel based alloy.
- 5 22. A fuel cell according to any one of claims 1 to 17 wherein the catalyst layer is prepared by a method according to any one of claims 18 to 21.
23. A fuel cell according to claim 21 wherein said catalyst layer has a thickness of between about one monolayer to about 20 monolayers.
24. A hybrid power source comprising a liquid feed fuel cell according to
10 any one of claims 1 to 13, 16, to 23, a DC to DC converter and a rechargeable battery.
25. A hybrid power source comprising a liquid feed fuel cell having a crossover current density of $15\text{mA}/\text{cm}^2$, preferably $5\text{mA}/\text{cm}^2$ or less, a DC to DC converter and a rechargeable battery.
- 15 26. A hybrid power source according to claim 24 or 25, comprising a fuel cell as defined in claim 1, a DC to DC converter and a rechargeable battery.
27. A hybrid power source according to any one of claims 24 to 26, wherein the number of cells in said fuel cell is two or three and said rechargeable battery is a lithium ion battery.
- 20 28. A fuel cell according to any one of claims 1 to 13, or 16 to 27, where the CO_2 produced during the operation thereof is released through a gas permeable hydrophobic matrix placed in the anode compartment or in the fuel tank.
29. A device for controlling the water return flow from the cathode side to the anode side in a fuel cell, comprising a water or fuel solution level sensor and
25 air or oxygen pressure control unit placed in the cathode compartment.
30. A fuel cell having an anode chamber with an anode and a fuel tank for providing said anode with fuel, a cathode chamber with a cathode and means for providing said cathode with oxygen in a given pressure, a solid electrolyte membrane disposed between said cathode and said anode, and a tank for water or
30 fuel solution, an air or oxygen pressure control unit and a sensor for sensing the

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level fuel solution in said fuel tank and means for controlling said pressure in response to said level of water or fuel.

31. A fuel cell according to claim 30, wherein the solid electrolyte membrane is as defined in claim 1.

5 32. A method for reducing crossover current in a fuel cell having an anode chamber with an anode and a fuel tank for providing said anode with fuel, a cathode chamber with a cathode and means for providing said cathode with oxygen in a given pressure, a solid electrolyte membrane disposed between said cathode and said anode, and a tank for water or fuel solution, an air or oxygen
10 pressure control unit and a sensor for sensing the level fuel solution in said fuel tank and means for controlling said pressure in response to said level of water or fuel, comprising the steps of:

(c) sensing the level of the water or fuel in the water or fuel tank;

(d) controlling the air or oxygen gas pressure in the cathode chamber to
15 increase as the level of water or fuel solution sensed in step (a) decreases;

thus reducing the crossover current.

33. A pump free direct oxidation fuel cell having a low crossover current density, wherein the fuel solution tank is directly attached to the anode chamber,
20 the fuel concentration is between 1% and 40% (w/w) and the ratio between the tank volume (in ml) and the electrode area, in cm^2 is between 3:1 and 30:1.

34. A pump free direct oxidation fuel cell according to claim 33 wherein said low crossover current density is of $15\text{mA}/\text{cm}^2$ or less.

35. A pump free direct oxidation fuel cell according to claim 34 wherein said
25 low crossover current density is of $5\text{mA}/\text{cm}^2$ or less.

36. A pump free direct oxidation fuel cell according to any one of claims 33 to 35, having a proton conducting membrane as defined in any one of claims 1 to 13.

37. An orientation independent direct oxidation fuel cell system having
30 (a) an anode chamber with an anode, fuel inlet and gas outlet;

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- (b) a cathode chamber with a cathode and oxygen or air inlet;
(c) an electrolyte membrane disposed between the anode and the cathode;
and
(d) a fuel tank connected to the anode chamber,
5 wherein

i) said fuel tank being divided by a movable barrier into two parts,
said first part of the fuel tank being capable of containing
fuel or fuel solution and connected to the anode chamber,
said second part of the fuel tank holding gas with pressure
10 greater than atmospheric pressure or having a closable gas
inlet;

ii) said gas outlet being closed with a gas permeable hydrophobic
matrix;

said barrier being capable of directing fuel or fuel solution from the fuel tank
15 to the anode chamber irrespective of the fuel cell orientation.

38. An orientation independent fuel cell according to claim 37, wherein said
second part of the fuel tank is filled with gas having a pressure above the
atmospheric pressure.

39. An orientation independent fuel cell according to claim 36 or 37, wherein
20 said second part of the fuel tank is capable of being fed with CO₂ evolving in the
anode chamber.

40. An orientation independent fuel cell according to any one of claims 36 to
39, wherein said movable barrier is a piston.

41. An orientation independent fuel cell according to any one of claims 36 to
25 39, wherein said movable barrier is a part of a bladder.

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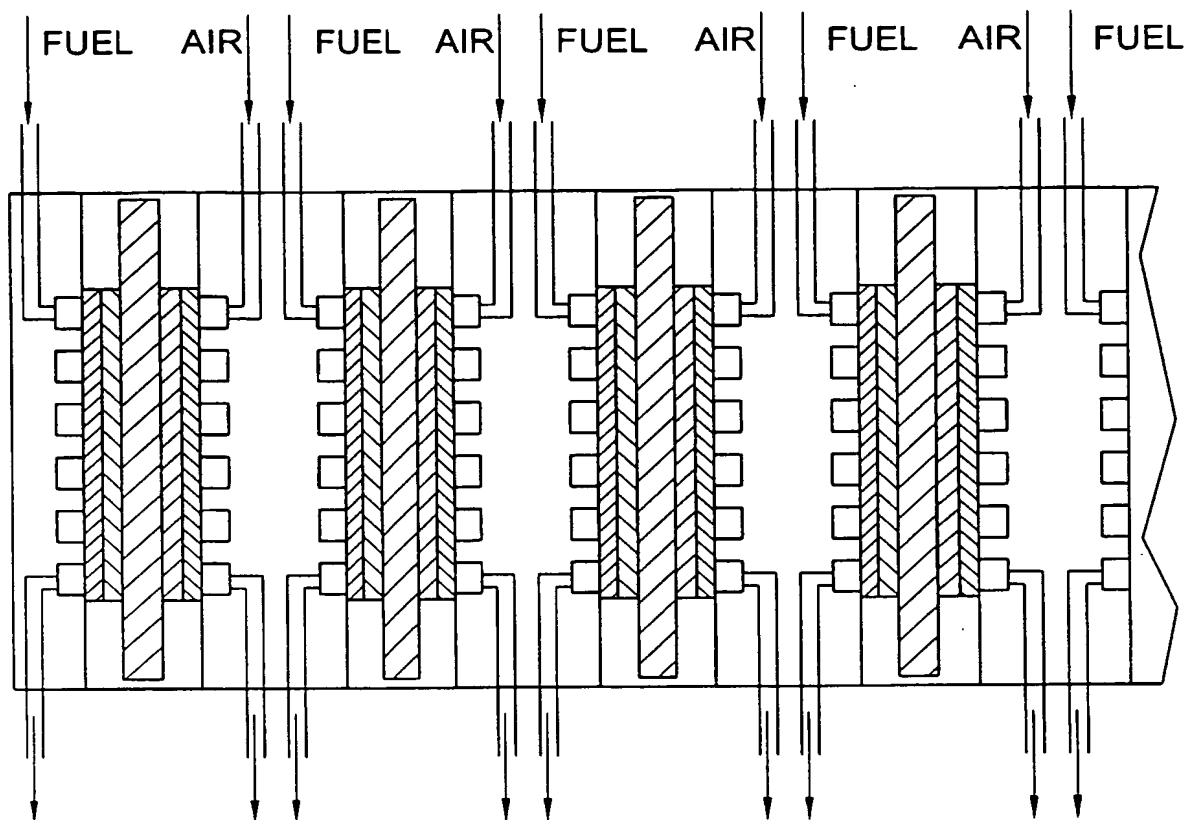


FIG. 1

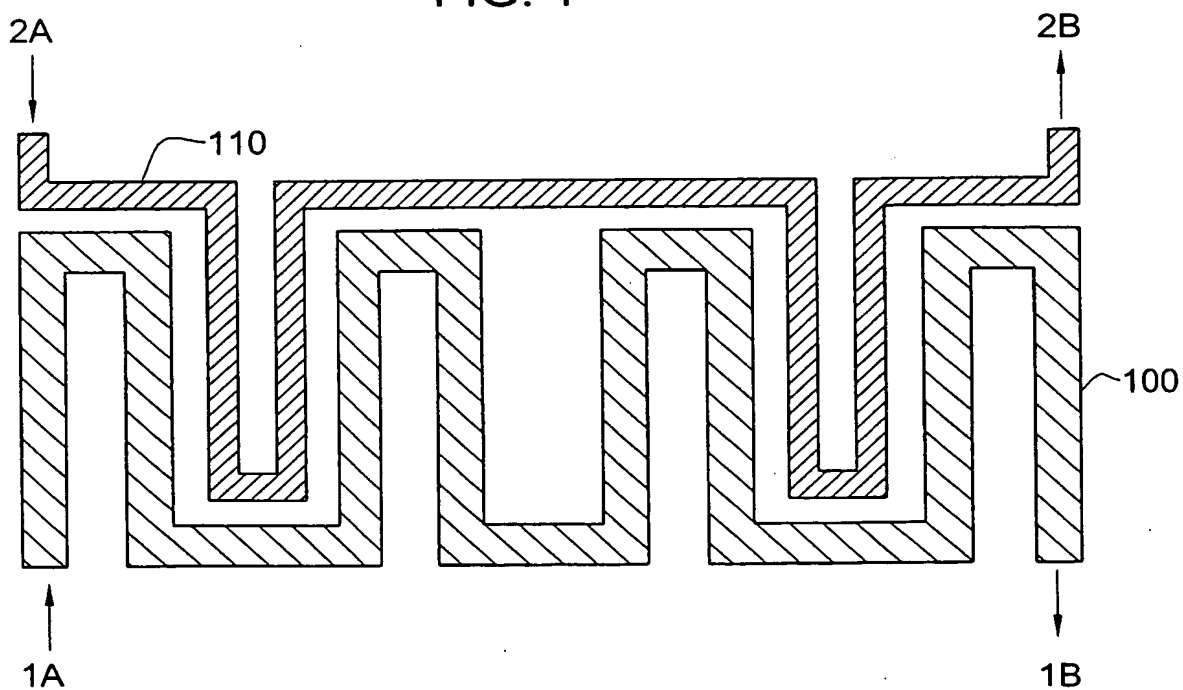


FIG. 2

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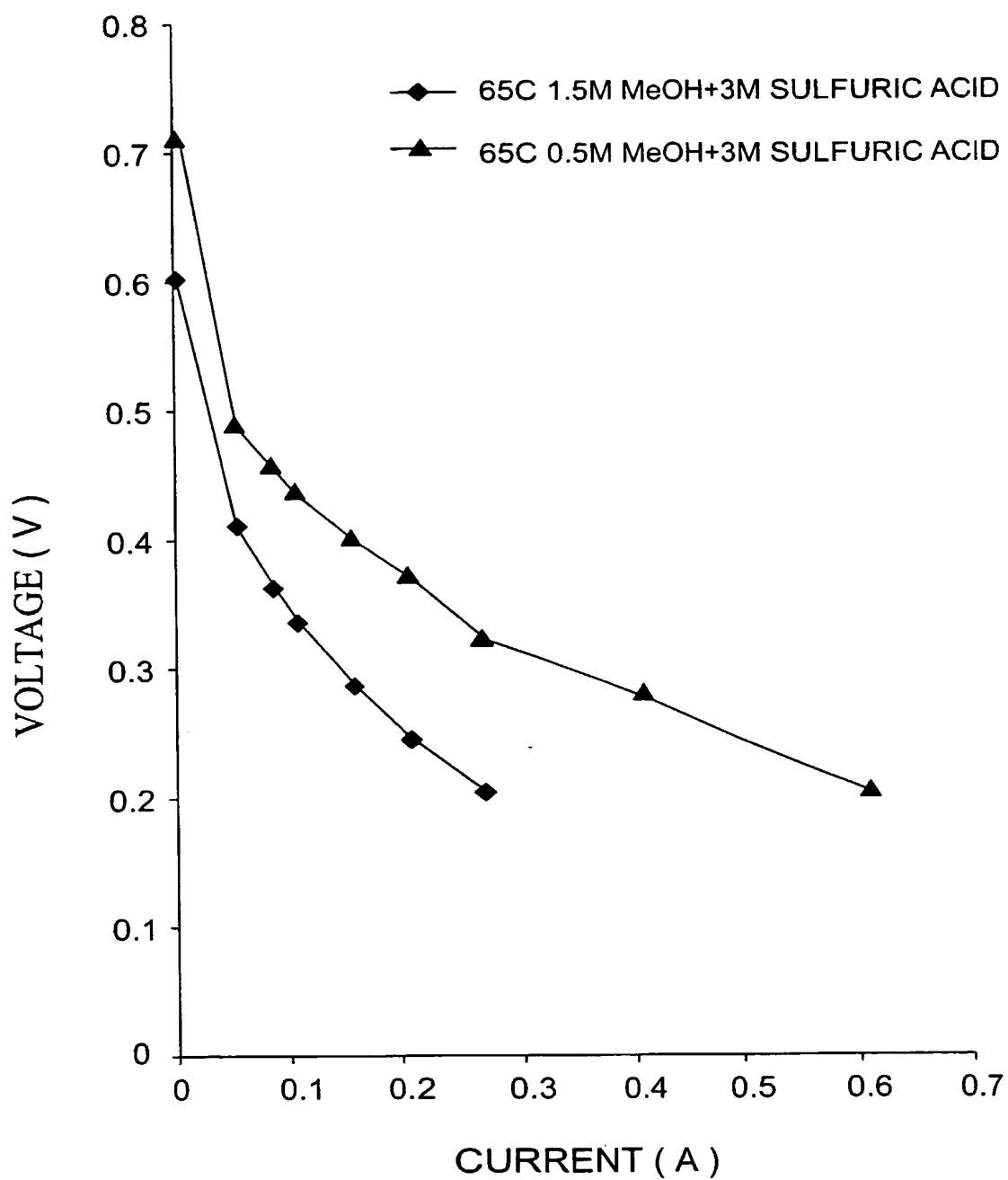


FIG. 3

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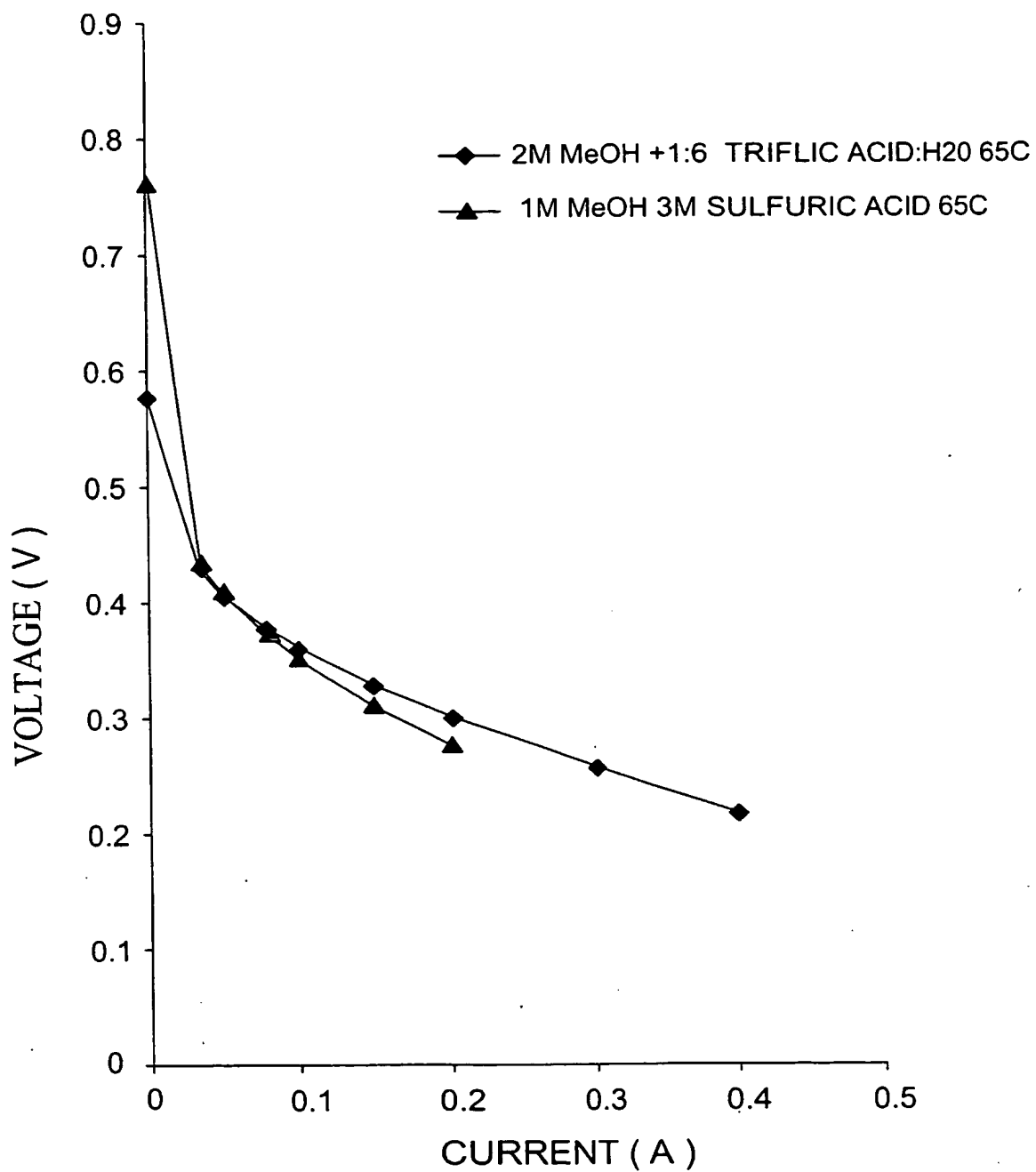


FIG. 4

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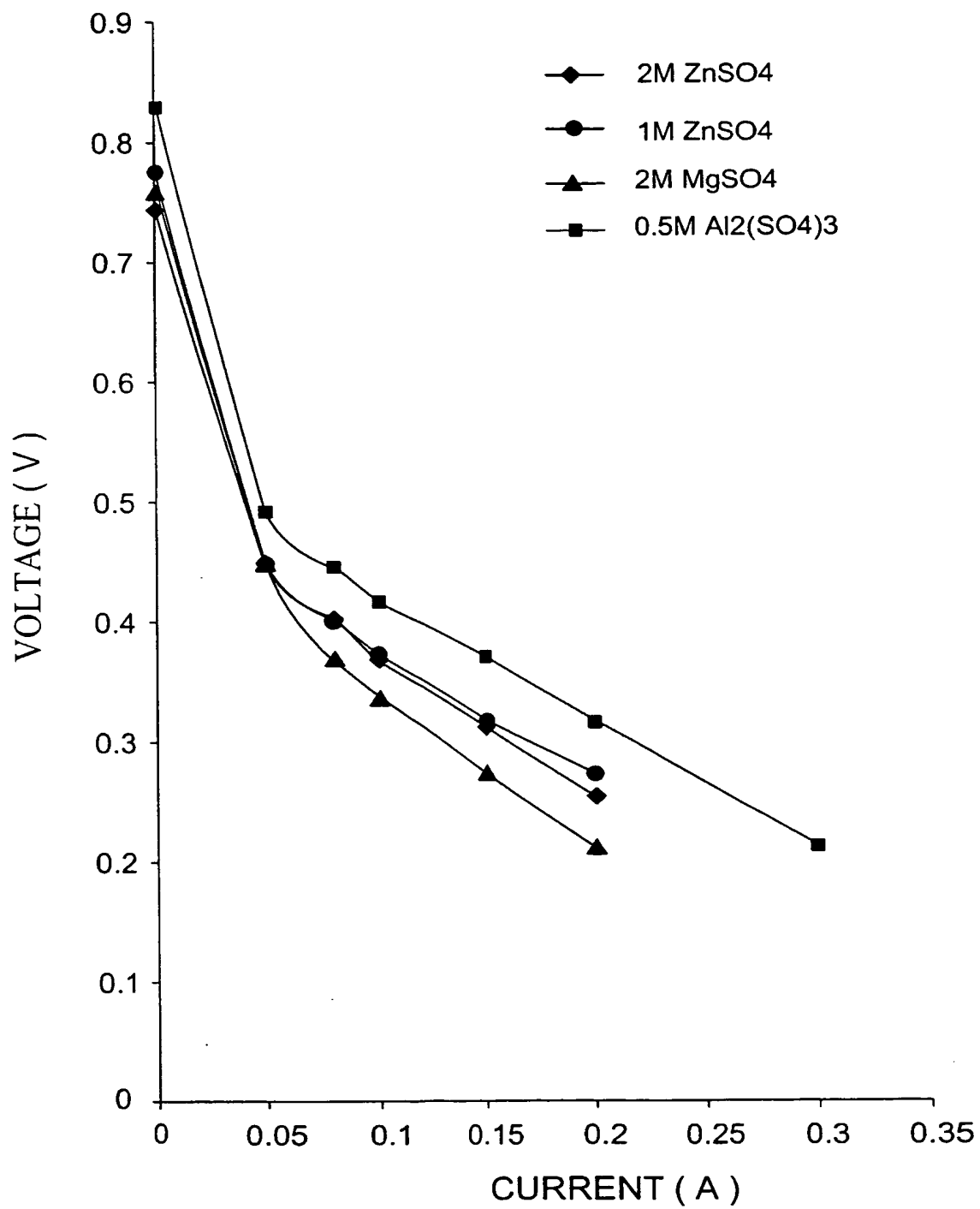


FIG. 5

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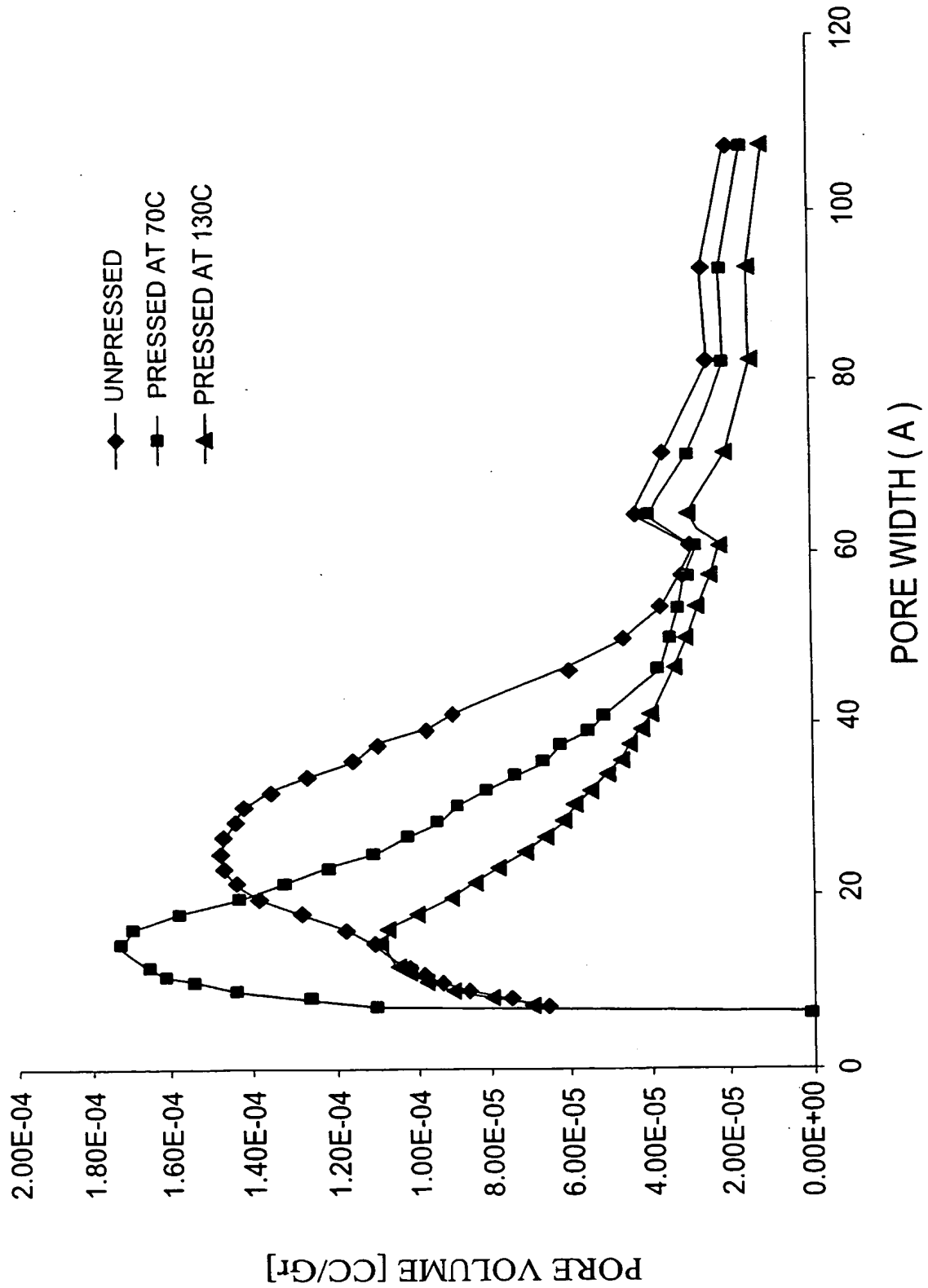


FIG. 6

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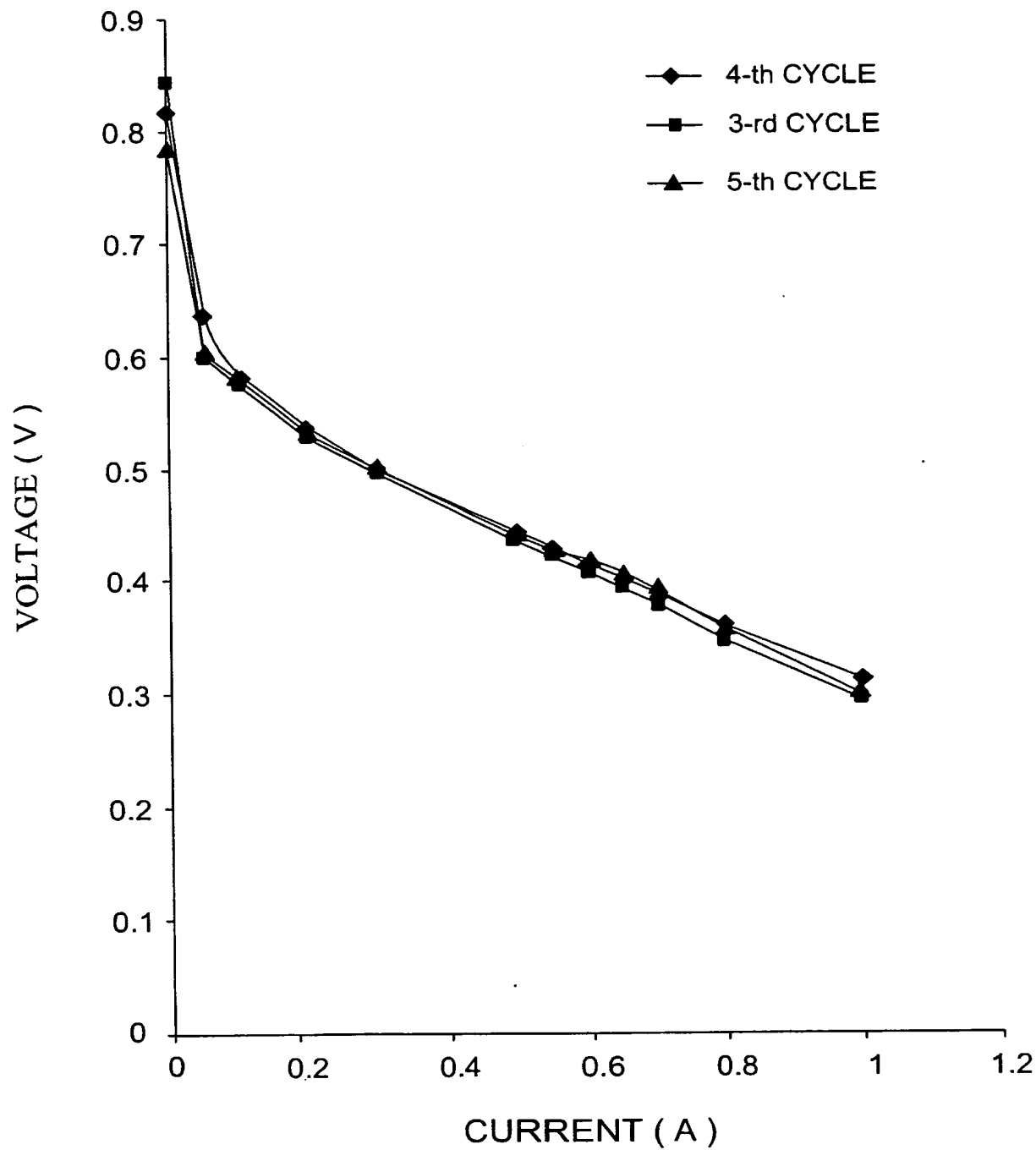


FIG. 7

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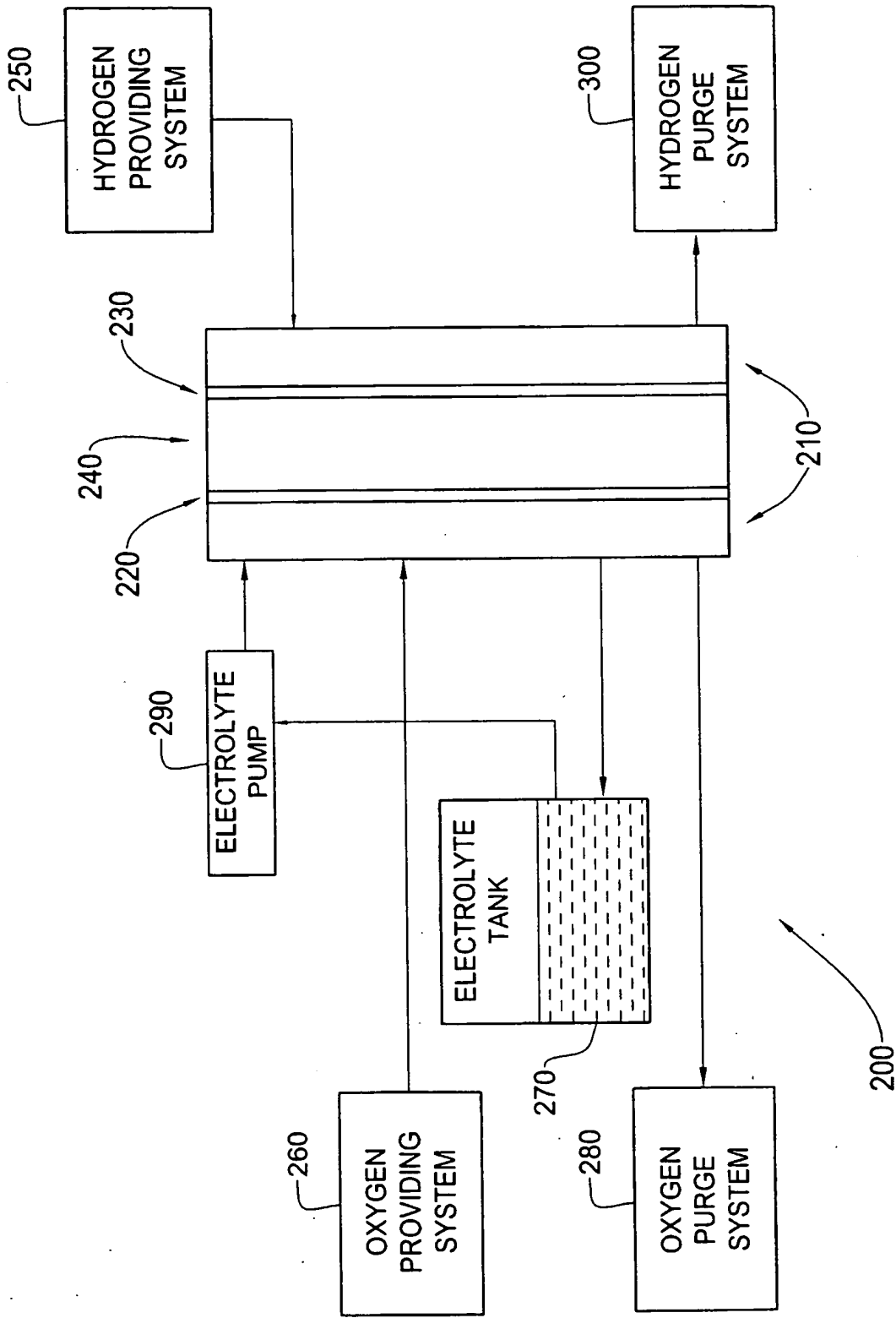


FIG. 8

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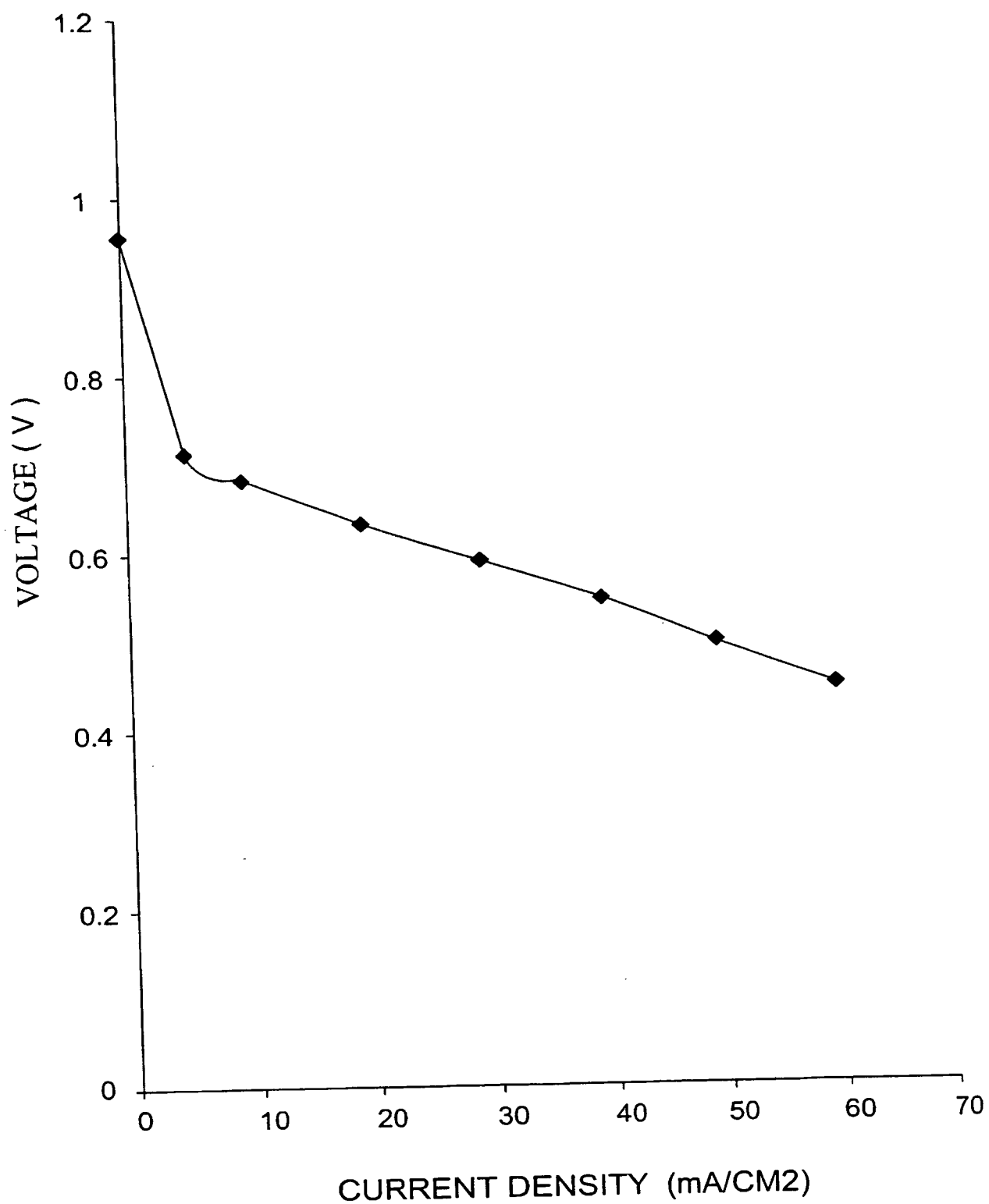


FIG. 9

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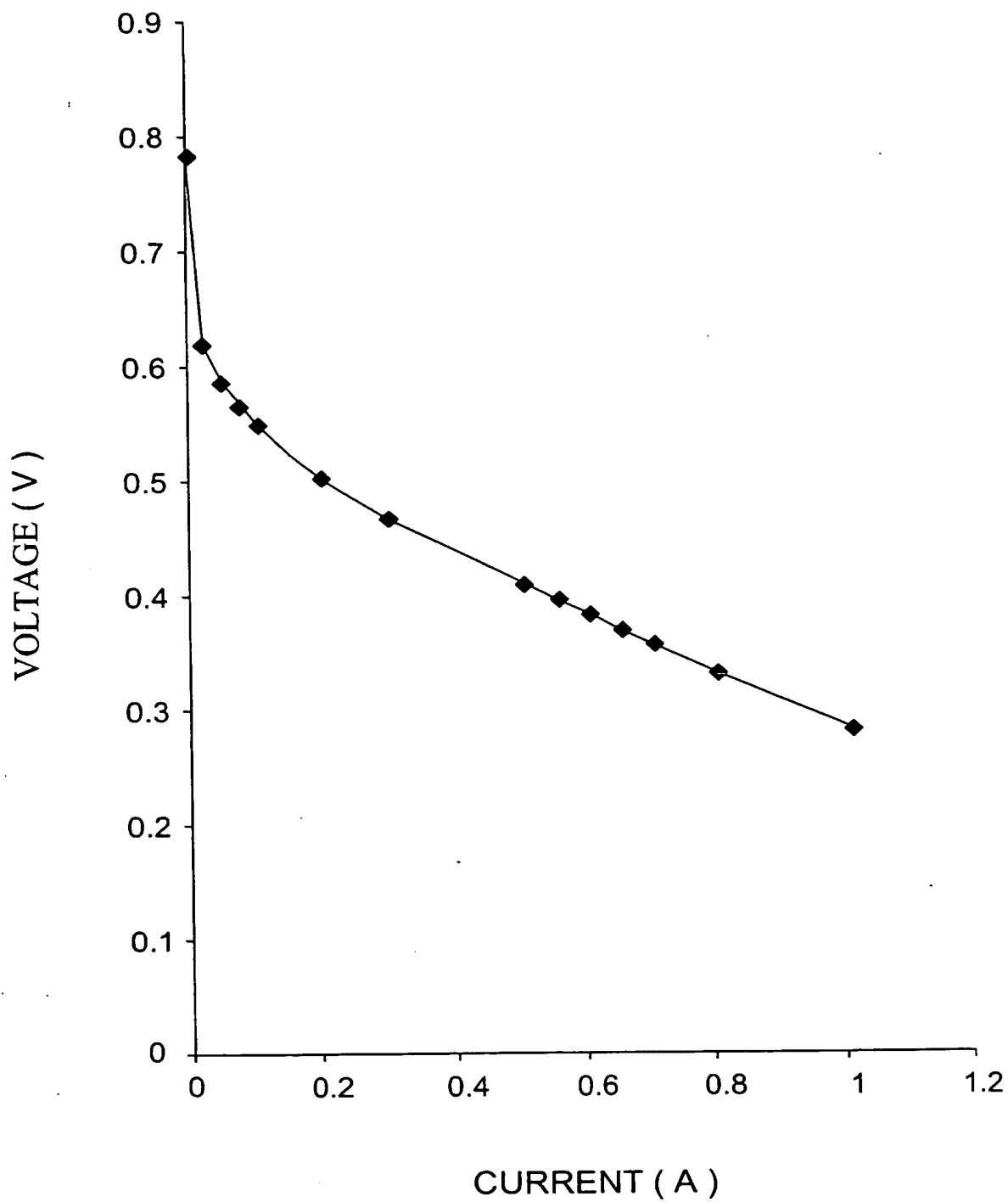


FIG. 10

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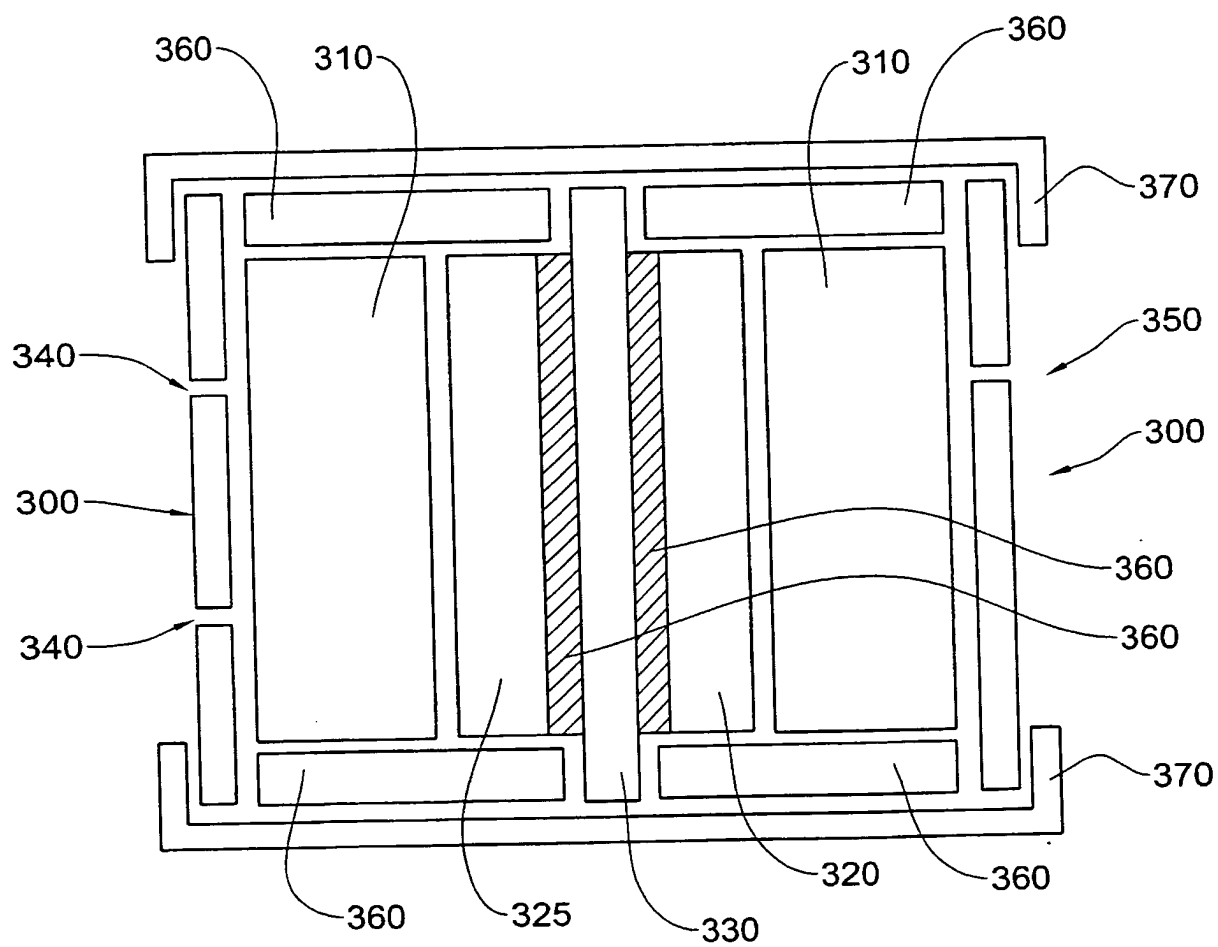


FIG. 11

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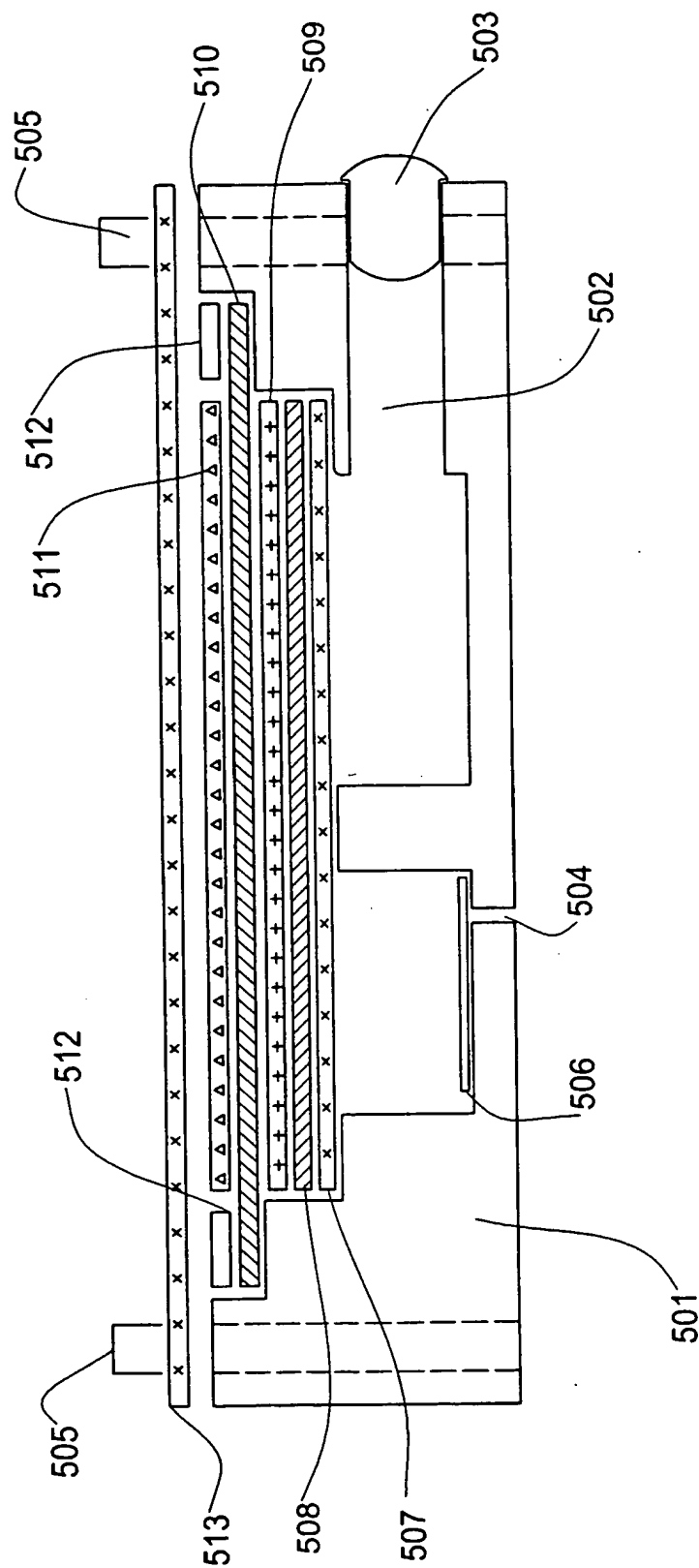


FIG. 12

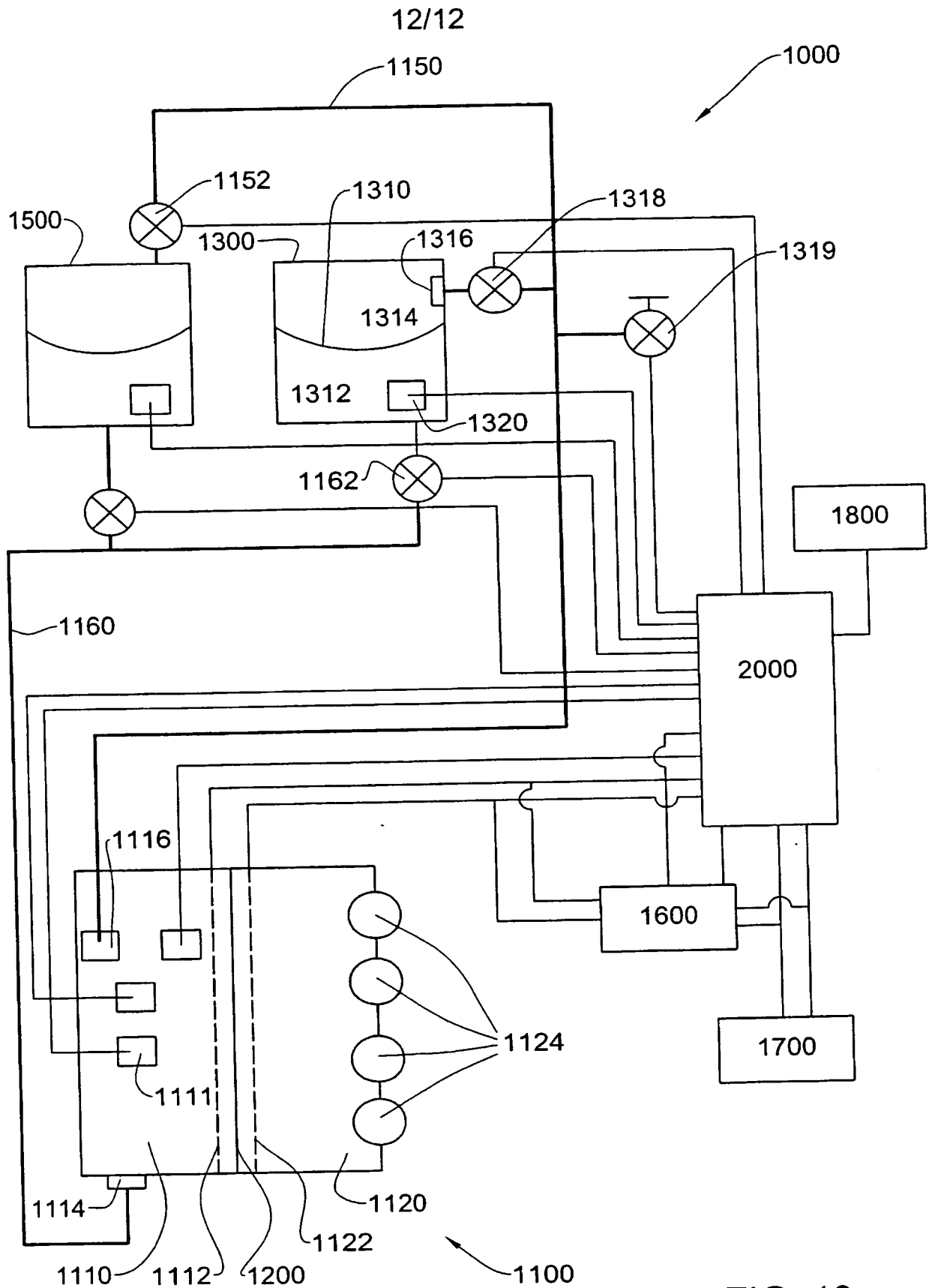


FIG. 13

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8/02, 8/10, 4/88, 8/04, B01J 23/56

H01M 8/16.

(74) Agent: REINHOLD COHN AND PARTNERS; P.O.
Box 4060, 61040 Tel Aviv (IL).

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(22) International Filing Date: 18 January 2001 (18.01.2001)

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(71) Applicant *for all designated States except US*: RAMOT
UNIVERSITY AUTHORITY FOR APPLIED RE-
SEARCH AND INDUSTRIAL DEVELOPMENT
LTD. [IL/IL]; P.O. Box 39296, 61392 Tel Aviv (IL).

(72) Inventors: and

(75) Inventors/Applicants *for US only*: PELED, Emanuel
[IL/IL]; 25 Hanotea Street, 40500 Even Yehuda (IL). DU-
VDEVANI, Tair [IL/IL]; 19 Carmeli Street, 52233 Ra-
mat Gan (IL). MELMAN, Avi [IL/IL]; 30 Kdoshei Kahir
Street, 58362 Holon (IL). AHARON, Adi [IL/IL]; 57 Ha-
hagana Street, 46325 Herzliya (IL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
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HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
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patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
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Published:

-- with international search report

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21 February 2002

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: FUEL CELL WITH PROTON CONDUCTING MEMBRANE

(57) Abstract: The present invention provides improved, low-cost fuel cells having reduced fuel crossover, reduced sensitivity to metal ion impurities and ability to operate under a broad range of temperatures. The invention further provides improved methods for catalyst preparation and a new integrated flow field system for use in H₂/O₂ fuel cells.

WO 01/54216 A3

INTERNATIONAL SEARCH REPORT

Intr. National Application No
PCT/IL 01/00055

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M2/16 H01M8/02 H01M8/10 H01M4/88 H01M8/04
B01J23/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, CHEM ABS Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PELED E ET AL: "A NOVEL PROTON-CONDUCTING MEMBRANE" ELECTROCHEMICAL AND SOLID-STATE LETTERS, US, IEEE SERVICE CENTER, PISCATAWAY, NJ, vol. 1, no. 5, 1 November 1998 (1998-11-01), pages 210-211, XP000785681 ISSN: 1099-0062 the whole document	1-7
A	---	16
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search

15 November 2001

Date of mailing of the international search report

23. 11. 01

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Gamez, A

INTERNATIONAL SEARCH REPORT

Intr. International Application No

PCT/IL 01/00055

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	----- PATENT ABSTRACTS OF JAPAN vol. 013, no. 487 (C-649), 6 November 1989 (1989-11-06) & JP 01 192742 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 2 August 1989 (1989-08-02) abstract	1-3,12
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INTERNATIONAL SEARCH REPORT

Intr. International Application No

PCT/IL 01/00055

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

national application No.
PCT/IL 01/00055

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-17, 22(partially), 24(partially), 25(partially), 26(partially), 27(partially), 28(partially), 31(partially), 36(partially)

A fuel cell comprising an anode side including an anode and means for providing fuel to anode, a cathode side including a cathode and a means for providing oxygen to cathode, and a solid electrolyte membrane disposed between said cathode and said anode, wherein said solid electrolyte membrane is a proton conducting membrane having pores with a diameter, which is smaller than 30 nm, said membrane comprising :

(i) 5% to 60% by volume, preferably 8% to 30% by volume of an electrically nonconductive inorganic powder having a good acid absorption capacity, said powder comprising nanosize particles;

(ii) 10% to 90% by volume, preferably 30% to 80% by volume of an acid or aqueous acid solution; and

(iii) 5% to 50% by volume, preferably 12% to 40% by volume of a polymeric binder that is chemically compatible with said acid, oxygen and said fuel.

2. Claims: 18, 19, 20, 21, 22(partially), 23 (partially), 24 (partially), 25 (partially), 26 (partially), 27(partially), 28(partially)

A method for preparing a catalyst layer for use in a fuel cell, said method comprising the steps of forming up to one monolayer of a catalyst on the surface of a nanosize inorganic powder, such monolayer serving as a nucleation site, forming additional one or more catalyst layers on the top of said first monolayer to obtain catalyst particles and subsequently binding the obtained particles to the carbon backing layer and/or to the proton conducting membrane.

3. Claims: 29, 30, 31 (partially), 32

A device for controlling the water return flow from the cathode side to the anode side in a fuel cell, comprising a water or fuel solution level sensor and air or oxygen pressure control unit placed in the cathode compartment.

4. Claims: 33, 34, 35, 36(partially)

A pump free direct oxidation fuel cell having a low crossover current density, wherein the fuel solution tank is directly attached to the anode chamber, the fuel concentration is between 1% and 40% (w/w) and the ratio

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

between the tank volume (in ml) and the electrode area, in cm² or less.

5. Claims: 37-41

An orientation independant direct oxidation fuel cell system having

(a) an anode chamber with an anode, fuel inlet and gas outlet;

(b) a cathode chamber with a cathode and oxygen or air inlet;

(c) an electrolyte membrane disposed between the anode and the cathode; and

(d) a fuel tank connected to the anode chambre, wherein

(i) said fuel tank being divided by a movable barrier into two parts, said first part of the fuel tank being capable of containing fuel or fuel solution and connected to the anode chamber, said second part of the fuel tank holding gas with pressure greater than atmospheric pressure or having a closable gas inlet;

(ii) said gas outlet being closed with a gas permeable hydrophobic matrix;

said barrier being capable of directing fuel or fuel solution from the fuel tank to the anode chamber irrespective of the fuel cell orientation.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claim 25 and claim 26 in so far as dependent on claim 25 relate to a product (liquid feed fuel cell) defined by reference to a desirable characteristic or property, namely a crossover current density of 15 mA/cm² or less. The claims cover all liquid feed fuel cell having this characteristic or property, whereas the application provides support within the meaning of PCT Article 6 and / or disclosure within the meaning of PCT Article 5 for only a very limited number of such fuel cell. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible.

Consequently, claims 25,26 have been partially searched, restricted to an hybrid power source comprising a liquid feed fuel cell according to any one of claims 1 to 13, 16 to 23 with a cross current density of 15 mA/cm² or less, a DC to DC converter and a rechargeable battery.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/IL 01/00055

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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